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[Authors alone are responsible for all opinions expressed in their Communications.]

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No. 33.

THE CHLORINATION OF DERIVATIVES OF o-ORSELLINIC ACID.

By T. J. NOLAN, B.A., D.Sc.,

AND

D. MURPHY, M.Sc.,

University College, Dublin.

[Read May 28. Published separately December 10, 1940.]

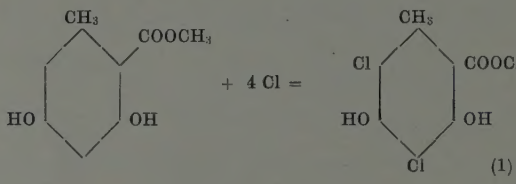
Introduction.

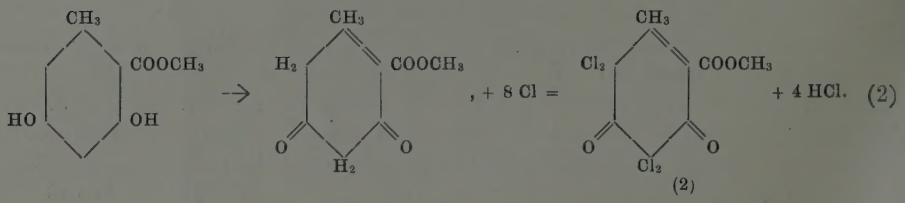
During investigations on the constitution of diploicin it was found by Nolan and Breen (private communication) that when diploicin is heated at 270–275° C. a product is obtained, m.p. 233–234° C., which has the formula $C_{15}H_8O_5Cl_4$, and which has been called by them nor-diploicin. When this product was heated with methyl alcoholic potash in an inert atmosphere at 40° C., a dichlor-dihydroxy toluic acid methyl ester was produced, m.p. 118–119° C. It was also found that, when diploicin was heated with a mixture of acetic and hydrochloric acids at 190–200° C., among the products obtained was a dichlor-dihydroxy toluene m.p. 120–121° C.

In the course of work on the constitution of gangaleoidin, Nolan and Davidson (private communication) isolated two products, a dichlor-dihydroxy toluic acid methyl ester identical with that obtained from diploicin, and a dichlor-dihydroxy toluic acid methyl ester methyl ether, m.p. 79° C. On the general assumption that both diploicin and gangaleoidin contain an orcinol structure, it was thought that these products might be dichlor-orsellinic acid methyl ester, dichlor-orcinol, and dichlor-orsellinic acid methyl ester methyl ether, respectively.

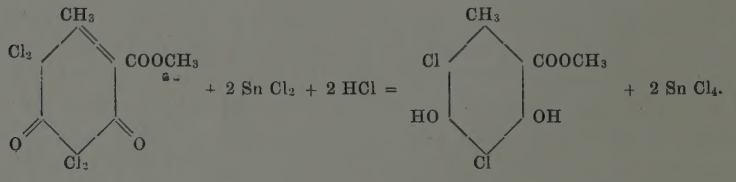
Calam and Oxford (J.C.S., 1939, p. 280) have prepared the 2 : 6 dichlor derivatives of methylation products of orcinol and p-orsellinic acid. 2 : 6 dichlor-orcinol and 2 : 6 dichlor-p-orsellinic acid methyl ester were not prepared by them, but they found for the melting point of 2 : 6 dichlor-orcinol dimethyl ether 133–134° C., and for 2 : 6 dichlor-p-orsellinic acid methyl ester dimethyl ether m.p. 86–88° C. Taking into consideration the fact that methylation usually produces substances of lower melting point than the originals, it seemed unlikely that the products obtained from diploicin and gangaleoidin were 2 : 6 dichlor derivatives. Accordingly it was decided to prepare 2 : 4 dichlor-orcinol, 4 : 6 dichlor-o-orsellinic acid methyl ester, and 4 : 6 dichlor-o-orsellinic acid methyl ester 5-methyl ether. The work has been extended to other derivatives of these substances. Comparison of the synthetic materials with the substances derived from diploicin and gangaleoidin indicates that the products got from these latter are, in fact, 2 : 4 dichlor-orcinol, 4 : 6 dichlor-o-orsellinic acid methyl ester, and 4 : 6 dichlor-o-orsellinic methyl ester 5-methyl ether.

The chlorination of o-orsellinic acid methyl ester with the theoretical amount of chlorine in chloroform solution gives the 4 : 6 dichlor derivative (1); when excess chlorine is used, a tetrachlor derivative is formed (2).

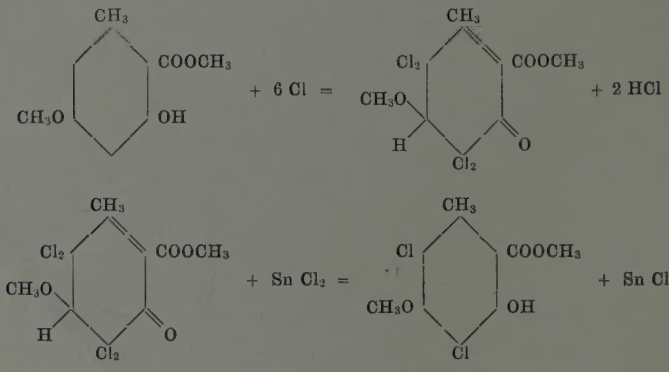




Reduction of the ketochloride (2) with stannous chloride in acetic acid produces the dichlor compound (1).



A similar reaction takes place with the monomethyl ether of o-orsellinic acid methyl ester.



EXPERIMENTAL.

2 : 4 dichlor-orcinol.

The orsellinic acid ethyl ester used in the preparation of 2 : 4 dichlor-orcinol was made according to the method of St. Pfau (*Helvetica Chimica Acta*, **16**, p. 283). The following improvement on Hesse's method (*Annalen*, **117**, p. 315) was employed to make 4 : 6 dichlor ethyl orsellinate :—1 g. of o-orsellinic acid ethyl ester was suspended in 20 c.c. of carbon tetrachloride, and a solution of chlorine in carbon tetrachloride added gradually, with vigorous shaking, until there was a distinct smell of residual chlorine. The whole was allowed to stand at room temperature for two hours and then filtered, and the white solid thus obtained crystallised from benzene m.p. 158–161° C.

The dichlor ethyl orsellinate is not readily hydrolysed by boiling with 5 per cent. alcoholic potash for 1½ hours; hydrolysis takes place more readily with aqueous potash. The following method was adopted :—0·5 g. of the dichlor ethyl ester was boiled with 15 c.c. 5 per cent. aqueous potash for two hours. The solution was then acidified and extracted with ether, and the solid recovered from the ether crystallised from benzene. The dichlor-orcinol thus obtained had m.p. 121° C.

3·960 mg. gave 6·360 mg. CO_2; 1·270 mg. H_2O.
5·300 mg. gave 7·850 mg. AgCl.
Found C = 43·8; H = 3·6; Cl = 36·6.
$C_7H_6O_2Cl_2$ requires C = 43·5; H = 3·1; Cl = 36·7.

Treatment of 2 : 4 dichlor orcinol in acetone solution with excess diazo-methane gave the dimethyl ether as an oil which it was not possible to crystallise.

4 : 6 dichlor-o-orsellinic acid methyl ester.

This substance was obtained in two ways, (1) by chlorination of o-orsellinic acid methyl ester with the theoretical amount of chlorine, and (2) by conversion of the ester into the ketochloride with excess of chlorine, and reduction of the ketochloride by means of stannous chloride to 4 : 6 dichlor-o-orsellinic acid methyl ester.

(1) 0·5 g. of methyl orsellinate was dissolved in 20 c.c. chloroform, and a solution of the theoretical amount of chlorine in carbon tetrachloride added slowly with cooling. The whole was allowed to stand for three hours, the solvent removed, and the somewhat oily residue crystallised from ligroin. The product was obtained as white needles m.p. 117° C. It crystallises with water of crystallisation, which appears on the sides of the flask when the material is

recrystallised from ligroin. The substance gives a purple reaction with ferric chloride.

3·787 mg. gave 5·790 mg. CO_2; 1·200 mg. H_2O.

4·620 mg. gave 4·990 mg. AgCl; 4·658 mg. gave 4·210 mg. AgI.

Found C = 41·7; H = 3·5; Cl = 26·7; OCH_3 = 11·9.

$C_7H_5O_2Cl_2(COOCH_3)\cdot\frac{1}{2}H_2O$ requires C = 41·5; H = 3·4; Cl = 27·3; OCH_3 = 11·9.

(2) 0·5 g. of methyl orsellinate dissolved in 20 c.c. chloroform was treated with 1·4 g. chlorine dissolved in 50 c.c. carbon tetrachloride, and the whole allowed to stand overnight. The solvent was evaporated, and the oily residue crystallised twice from ligroin, and finally from benzene. The product was thus obtained as white needles m.p. 132–134° C. On standing it appeared to lose solvent of crystallisation, and before analysis was dried in vacuum for a prolonged period. It gives no reaction with ferric chloride; it is the keto-chloride.

4·160 mg. gave 5·190 mg. CO_2; 0·660 mg. H_2O.

5·590 mg. gave 9·860 mg. AgCl; 5·145 mg. gave 3·640 mg. AgI.

Found C = 34·0; H = 1·8; Cl = 43·6; OCH_3 = 9·3.

$C_7H_3O_2Cl_4(COOCH_3)$ requires C = 33·8; H = 1·9; Cl = 44·4; OCH_3 = 9·7.

0·4 g. of the ketochloride dissolved in 15 c.c. acetic acid was treated in the cold with 1 g. stannous chloride dissolved in a few c.c. of 20 per cent. hydrochloric acid; the whole was well shaken and then diluted with water. The precipitate was collected, dried, and crystallised from ligroin, from which it separated in white needles, m.p. 117–118° C., not depressed on admixture with dichlor methyl orsellinate. It also gave the purple ferric chloride reaction of the latter.

4 : 6 dichlor-o-orsellinic acid 3 : 5 dimethyl ether.

0·2 g. 4 : 6 dichlor ethyl orsellinate was dissolved in 10 c.c. acetone and treated with excess ethereal diazomethane solution. On evaporation of the solvent after prolonged standing, the methyl ester dimethyl ether was obtained as an oil. This oil was boiled for two hours with 10 c.c. of 5 per cent. aqueous potash, the resulting solution acidified, and the precipitate crystallised from ligroin. The acid, which gives no reaction with ferric chloride, was obtained as white needles m.p. 135–136° C.

3·97 mg. gave 6·54 mg. CO_2; 1·310 mg. H_2O.

4·15 mg. gave 4·41 mg. AgCl; 3·96 mg. gave 6·850 mg. AgI.

Found C = 44·9; H = 3·7; Cl = 26·3; OCH_3 = 22·8.

$C_7H_3Cl_2(OCH_3)_2(COOH)$ requires C = 45·3; H = 3·8; Cl = 26·8; OCH_3 = 23·4.

4 : 6 dichlor-o-orsellinic acid methyl ester 5 : methyl ether.

Orsellinic acid methyl ester 5 : methyl ether was prepared by treating orsellinic acid in acetone with the theoretical amount of diazomethane in ether. After removal of the solvents the resulting product was crystallised from dilute methyl alcohol and was obtained as fine white needles m.p. 63–65° C. The dichlor derivative was obtained in two ways, (1) by chlorination of o-orsellinic acid methyl ester 5 : methyl ether with the theoretical amount of chlorine, and (2) by conversion of the ester ether into the ketochloride with excess of chlorine, and reduction of the ketochloride by means of stannous chloride to 4 : 6 dichlor-o-orsellinic acid methyl ester 5 : methyl ether.

(1) 1 g. of ester dissolved in 20 c.c. chloroform was treated with slightly more than the theoretical amount of chlorine in carbon tetrachloride. The whole was allowed to stand overnight, the solvent removed, and the residue crystallised from dilute methyl alcohol. The product was obtained as white needles m.p. 79–81° C.

3·657 mg. gave 6·050 mg. CO_2; 1·280 mg. H_2O.
4·200 mg. gave 4·570 mg. AgCl; 3·792 mg. gave 6·850 mg. AgI.
Found C = 45·1; H = 3·9; Cl = 26·9; OCH_3 = 23·9.
$C_7H_4OCl_2(OCH_3)(COOCH_3)$ requires C = 45·3; H = 3·8; Cl = 26·8; OCH_3 = 23·4.

(2) 0·4 g. of ester in 10 c.c. carbon tetrachloride was treated with 0·46 g. chlorine in carbon tetrachloride, continuous stirring being maintained during addition of the latter. After standing for two hours, the solvent was removed by evaporation at air temperature. The residue was first crystallised from ligroin, which gave a rather oily product, and then from methyl alcohol. White needles were obtained which gave no reaction with ferric chloride, and which had m.p. 144–146° C.

3·940 mg. gave 5·290 mg. AgI.
5·586 mg. gave 9·320 mg. AgCl; 4·014 mg. gave 6·980 mg. AgCl.
Found Cl = 41·3; 43·0; OCH_3 = 17·7.
$C_7H_4OCl_4(OCH_3)(COOCH_3)$ requires Cl = 42·3; OCH_3 = 18·45.

A sample of the crude ketochloride was dissolved in acetic acid, and reduced in the cold with stannous chloride in 20 per cent. hydrochloric acid. On dilution a white precipitate was obtained, which, on being crystallised twice from 70 per cent. methyl alcohol, was obtained as white needles, m.p. 79–80° C., not depressed when mixed with 4 : 6 dichlor o-orsellinic acid methyl ester methyl ether prepared by method (1).

No. 34.

"STUDIES IN PEAT."

PART 9.

THE CEROTIC AND CARBOCERIC ACID FRACTIONS OF MONA WAX.

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Chemical Department, University College, Cork.

[Read NOVEMBER 26. Published separately DECEMBER 10, 1940.]

RYAN and Dillon (Sci. Proc. Roy. Dub. Soc., **12**, 202, 1909) examined a commercial wax, called Montana wax. It was probably of French or German origin. They isolated from it Montanic acid by precipitation of the acid, to which they assigned the formula $C_{28}H_{56}O_2$. In the same paper, they described an examination of a sample of wax from Irish lignite (Co. Antrim), and suggested that the free acid from this wax was also Montanic acid.

This Irish lignite wax and Irish peat wax (Mona wax) differ considerably in origin and constants. The lignite wax was stated (Ryan and Dillon, *loc. cit.*) to have an acid value of 70·28, and to contain only a trace of ester. The acid value of Mona wax was 46, and the ester value 52. A difference in chemical constituents might then be expected.

Roginskaya (J. Applied Chem., U.S.S.R., **9**, 108, 1936) has reported the presence of $C_{29}H_{58}O_2$, $C_{28}H_{56}O_2$ and $C_{27}H_{54}O_2$ in an alcohol-soluble Russian peat wax. Titow (Brennstoff-Chemie, **13**, 266, 1932) has examined a "benzin"-soluble wax from the same peat, and has isolated from it $C_{27}H_{54}O_2$ and $C_{25}H_{50}O_2$.

Holde (Kohlenwasserstofföle und Fette, 1924, **5**, 763) from a consideration of the theory of fat formation proposed by Buchner and Meisenheimer (Ber. **41**, 1414, 1908) concluded that only n-fatty acids with an even number of carbon atoms can occur in nature. The X-ray analyses of Francis, Piper and Malkin (Proc. Roy. Soc. London, 128, A, 214, 1930) fully supported his conclusion. They found that all the fatty acids isolated from natural sources are mixtures of n-fatty acids containing an even number of carbon atoms. The investigations described in the present paper indicate that the main acid fractions from Mona wax contain cerotic ($C_{26}H_{25}O_2$) and carboceric ($C_{27}H_{54}O_2$) acids.

It is intended in further work on the wax acids to obtain fractions large enough for repeated re-fractionation. Then, by using the most efficient fractionating equipment, a separation into single acids might be accomplished.

Experimental.

(1) *The extraction, description and properties of the crude wax.*—The sample of wax used in this investigation was obtained from Kerry peat. The wax was extracted by means of hot commercial X-2 petrol (10 per cent. aromatic content; B.P. 90°–100° C.) under pressure on a small-scale plant. It was dark-brown to black in colour, and could scarcely be marked with the finger-nail.

Besides wax, the petrol also extracted some resin and bituminous matter, so that the wax was contaminated with these products. The wax could be freed from resin due to the solubility of the latter in cold ethyl alcohol. The removal of the resin from the wax was very desirable, but, as some free wax acids and lower melting wax esters may be soluble in the alcohol, the wax was not treated with this solvent.

The percentage resin was estimated by refluxing 20 g. powdered wax with 200 c.c. of 95 per cent. ethyl alcohol for two hours. By chilling the alcohol and filtration the wax is removed. On evaporating the solvent the resin is obtained as a dark brown mass of soft consistency. The resin-content was found to be 9·8 per cent. An investigation of the resin is at present in progress.

The following were the properties of the wax (as extracted) :—

Saponification value	98
Acid value	46
Ester value	52
Iodine value (Wijs)	30
Softening Point	70°–71° C.

(2) *Saponification of Wax.*—The first step in the separation of the acids was the saponification of the wax esters. The hydrolysis was carried out with concentrated potassium hydroxide solution under reflux.

After saponification the acids were present as potassium salts. Many workers isolated the acids as potash salts, and freed them from unsaponifiable matter by extracting with light petroleum, benzene, acetone, etc. Chibnall and his co-workers, however, have pointed out that the potassium salts of the fatty acids become increasingly soluble in the above solvents with increase of chain length. They suggest that the higher fatty acids (in waxes, etc.) should be converted into the very insoluble calcium salts before extracting non-soapy material. The calcium salts were, therefore, precipitated.

50 g. of wax was dissolved in 500 c.c. of benzene. A solution of 20 g. potassium hydroxide in 300 c.c. of 95 per cent. ethyl alcohol was added, and the mixture boiled for six hours to complete saponification. A boiling solution of 75 g. of anhydrous calcium chloride in 280 c.c. 95 per cent. ethyl alcohol was added in small quantities with vigorous shaking. The mixture was then boiled for an hour to complete the reaction.

On standing, the calcium soaps settled to the bottom as an almost white layer. The dark supernatant solution of unsaponifiable matter was decanted

off. The soaps, after drying down on a steam bath, were ground to a fine powder, and the unsaponifiable matter extracted in soxhlets with benzene till the solvent was colourless. On drying, the calcium salts were obtained as a white powder. The unsaponifiable portion, consisting of alcohols,[1] hydrocarbons, and bituminous material, was recovered by evaporating the benzene. It was a rather soft brown solid.

(3) *Liberation of the acids.*—Initial treatment of the powdered calcium soaps with hydrochloric acid solution gave rise to troublesome emulsions. The following method was found to give the best results:—

50 g. of the powdered calcium soaps were heated with 200 c.c. glacial acetic acid for two hours. The contents of the flask were then poured into a large excess of water, when the free acids and any unchanged calcium salt rose to the surface. The acetic acid water layer was removed by means of a siphon. Fresh water was added, and the mixture boiled till the acids appeared as a dark brown layer, floating on the water. They were removed and heated with hydrochloric acid solution (2 parts water: 1 part conc. hydrochloric acid) to complete the conversion of the calcium soaps to free acids. On cooling, the acids, in the form of a hard cake, were removed and heated repeatedly with water till free from mineral acid.

Yield of crude acids from wax	45% (mean value).
Acid value	105.
Iodine value (Wijs)	21.
Softening point	73°–75° C.

(4) *Esterification.*—Tropsch and Kreutzer (Brennstoff-Chemie, **3**, 177, 193–212, 1922) found that very poor yields of ester were obtained on heating the crude acids from Montan wax with excess methyl alcohol and a little concentrated sulphuric acid. This was due to the small solubility of the acids in the alcohol. The same difficulty was encountered in the present investigation.

The acids were then esterified in small amounts. 20 g. of the crude acids were refluxed with 600 c.c. of methyl alcohol and 20 c.c. concentrated sulphuric acid for 8 hours. The solution assumed a dark brown-red coloration. On decantation and cooling, the ester separated as a pale yellow mass. The residue was refluxed with more methyl alcohol and sulphuric acid till no further extraction took place. By evaporating the alcohol solution down to approximately 100 c.c. and pouring into a large volume of cold water, all the ester was obtained. On boiling the water, the ester melted and formed a brown layer on top. It was freed from sulphuric acid by the usual procedure.

When cold, the cake of esters was separated and kept at 100°–105° to remove water.

Acid value of esters	10.
Iodine value (Wijs)	16.
Softening Point	65°–66° C.

[1] Results of a separate investigation at University College, Cork (with Miss T. Power), indicate the presence of ceryl alcohol ($C_{26}H_{54}O$). This work will be published later.

As the acid value was due to the presence of some unesterified acid, a re-esterification was performed using the above method again. The residue, when freed from mineral acid, was very hard shiny black pitch-like material. It had no acid value, and constituted 47 per cent. of the total crude acids (i.e., of the crude acids 53 per cent. were esterified).

The colour of the methyl esters (47 g.) at this stage was a warm brown. A straight vacuum distillation (2 mm.) was performed on them in order to free them from the dark material present. The esters collected in the receiver as a yellow-coloured waxy solid (33 g.), the residue being a dark brown mass of resinous appearance. At the first signs of decomposition (fuming) the distillation was stopped. The acid value of the distilled ester was 22, indicating that some decomposition had taken place. The esters were boiled up with 1,000 c.c. methyl alcohol and 25 c.c. of concentrated sulphuric acid. On collecting the esters in the usual manner, the acid value was found to have dropped to 2·8.

(5) *Fractionation of Methyl esters.*—It was decided to use the Longenecker column (J.S.C.I., 1937, 199 T), which embodies many of the improvements in modern fractionation technique. The flask containing the 27 g. of the esters was fused on to the bottom of the column, and was heated by means of a lead-bismuth metal bath. The fractions were collected by means of a Perkin triangle, which was kept at 60°–65° C. The pressure was measured on a MacLeod gauge repeatedly during the distillation. It varied between 1·5 mm. and 2 mm.

Fraction.	B.Pt. °C.	Yield (g.).	M. Pts. (Incipient Fusion-Complete Fusion).
1	150–172	2·3	Liquid
2	172–183	2·5	40·5–42
3	183–190	2·45	46 –47
4	190–200	4·15	53 –54
5	200–215	5·8	57 –58
6	215–223	4·65	59·6–61

Total = 21·85 g. (80 per cent. yield).

As decomposition had taken place in the preliminary distillation resulting in the production of some free acids, the acid number of each fraction was determined. It varied from 1–3, indicating that very little decomposition had occurred in this actual distillation.

The first fraction consisted of a pale yellow liquid. The others solidified to yellow waxy solids. To ascertain if fractionation had taken place the acids from fractions 2 and 5 were analysed.

Fraction 2 ...	Found 77·0% C.	12·9% H.
$C_{22}H_{44}O_2$ requires	77·6% C.	12·9% H.
Fraction 5 ...	Found 79·13% C.	13·11% H.
$C_{26}H_{52}O_2$ requires	79·02% C.	13·17% H.

This indicates that a separation into higher and lower constituents had been accomplished. Fractions 5 and 6 were then examined.

Fraction 5 (5·8 g.).—A sample of ester after decolorising with "actibon" neutral grade charcoal (which was first extracted with hot alcohol) separated from alcohol in a white semi-crystalline form.

Analysis.	Found 79·13% C.	13·11 % H.
Calculated for $C_{27}H_{54}O_2$ (Methyl Cerotate)	79·02% C.	13·17 % H.

The melting point of this methyl ester was 59° C. Francis, Piper and Malkin (*loc cit.*) isolated cerotic acid from beeswax, and found its methyl ester to melt at 60° C.

Hydrolysis of the ester was carried out by means of N/2 alcoholic potassium hydroxide solution. The free acid was then obtained by heating the potassium soaps with excess hydrochloric acid solution for two hours. The acid formed a light brown-coloured layer on the surface. It was freed from mineral acid, and decolorised by treatment with charcoal.

After two crystallisations from ethyl acetate, the acid was obtained in glistening flaky plates with a "mother of pearl" appearance.

Analysis.	Found 78·65% C.	13·06% H.
Calculated for $C_{26}H_{54}O_2$	78·78% C.	13·13% H.

On drying in vacuo for six hours, the acid had a melting point (open capillary tube) of 78·5° C., and an acid value of 142·8. The calculated acid value for $C_{26}H_{52}O_2$ is 141. Francis *et al.* found the cerotic acid they isolated to have a melting point of 78° C. These investigators, by X-ray analysis, found this acid to be actually a mixture of $C_{26}H_{52}O_2$ and $C_{28}H_{56}O_2$. It is highly probable that "cerotic acid" from Mona wax is a similar mixture. Its low melting point proves that it is not identical with synthetic $C_{26}H_{52}O_2$, which has a melting point of 88·2° C.

Fraction 6 (4·65 g.).—The ester was purified by treatment with charcoal and recrystallisation.

Analysis.	Found 79·04% C.	12·85% H.
Calculated for $C_{28}H_{56}O_2$ (Methyl Carbocerate)	79·24% C.	13·21% H.

The melting point of the methyl ester was 63°–64° C.

Tropsch and Kreutzer (*loc. cit.*) and Titow (*loc. cit.*) have found the melting point of the methyl ester of carboceric acid to be 63° C.

The acid separated from acetic ester in glistening flakes with a "mother of pearl" appearance.

Analysis.	Found 78·70% C.	12·79% H.
Calculated for $C_{27}H_{54}O_2$	79·02% C.	13·17% H.

The same workers found the melting point of carboceric acid to be 82° C. The acid from fraction 6 had a melting point 81°–81·5° C. The low melting point of the acid indicated that a mixture of acids was present.

Roginskaya (*loc. cit.*) and Titow (*loc. cit.*) have also obtained fatty acids with an uneven number of carbon atoms. This probably indicates, as in our example, a mixture of two fatty acids rather than one in accordance with Holde's supposition.

Further work is in progress on this problem, and a number of the fractionated samples will be studied by means of X-ray analysis.

Summary.

A sample of Mona wax was saponified. The acids were separated by means of their insoluble calcium salts. The latter were decomposed by mineral acid to give a mixture of crude acids. These were converted into their methyl esters, which were fractionated by means of the Longenecker column.

The two large fractions of highest boiling point were investigated. They were found to consist mainly of cerotic ($C_{26}H_{52}O_2$) and carboceric ($C_{27}H_{54}O_2$) acids respectively.

The authors desire to thank Mr. J. A. Emlyn, F.I.C., for assistance in connection with the fractionation of the methyl esters.

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No. 35.

SALMON OF THE BALLISODARE RIVER.

II.—AGE AND GROWTH.

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[Read November 26, 1940. Published separately January 13, 1941.]

The salmon fishery of the Ballisodare River is of great interest to workers engaged on research on freshwater fishes, because, but for the intervention of man, no salmon could possibly have ascended the river and reproduced its kind. Fortunately, the early history of the fishery can be followed in fairly great detail, and in a previous contribution to the Scientific Proceedings of the Society (Went, 1940) an account has been given of the alterations which were necessary before salmon could ascend the river and of the early history of the fishery.

In 1938 and 1939 an opportunity was taken to collect sets of scales and data from salmon captured in the net fishery in the tideway of the Ballisodare River in order that the present life history of the salmon of the river might be investigated and compared with the life history in the early days of the fishery as deduced from the records.

Material.

The material used in this investigation consisted of 1,090 satisfactory sets of scales and measurements of salmon taken in the tidal portion of the Ballisodare River at the three netting stations, the positions of which have already been indicated (Fig. 1, Went, 1940). The number of fish sampled in each month is given in the following table:—

Month.	*No. of fish sampled.*	
	1938.	1939.
March	5	–
April	17	40
May	43	53
June	347	297
July	179	109
Total ...	591	499

Examination of the above table and of the figures for the total catch and weight in each month reveals that the numbers of fish sampled in each month were fairly adequate and representative of the total catches. Unavoidable fluctuations in the percentage of fish sampled were noted, but by suitable arithmetical manipulations the data supplied can be used to obtain a fairly

good picture of the incoming populations in the two years in question. Figures given in the various tables in the Appendix include, where possible, the weighted results. There appears to be a slight tendency to select the larger members of the catch during each season investigated, but this selection does not materially affect the monthly averages given in the Appendix. The legal season for netting of salmon in the tidal waters of the Ballisodare River is from the 4th March to the 11th September, but runs of salmon into the river are almost restricted to the period from late March until about the end of July. The sample investigated might, therefore, be expected to give a very complete picture of the incoming populations in the years in question.

Methods.

All fish examined were measured from the tip of the snout to the fork of the tail, and the length was recorded to the nearest quarter of an inch.

Smolt ages.

The distribution of the smolt ages in each age group is given in Table 1 (see Appendix for all tables). The bulk of the fish migrated as one- and two-year-old smolts; the one-year smolts are quite important (22·9 per cent. in 1938 and 18·8 per cent. in 1939). This is a relatively high proportion of one-year smolts, similar to that which has already been described for the River Shannon (Went, 1938). Few rivers which have been adequately investigated have shown such a high proportion of one-year smolts as the Ballisodare River and the River Shannon. Examination of Table 1 reveals that the proportion of young smolts (one-year smolts) increases with an increase in the time spent in the sea.

The monthly changes in the percentage of one-year smolts were calculated, and it appears that in 1939 there was a decrease in the proportion of one-year smolts as the season progressed. This is contrary to the conditions found in the case of the River Shannon.

Age Groups.

The fish whose scales were satisfactory for age determinations were divided into four groups of maiden or unspawned fish, and one group containing those fish which had spawned previously. The percentage of each age group in the year's catch is given in Table 2.

Grilse formed 81·3 per cent. and 82·6 per cent. of the total catch in 1938 and 1939, respectively. Large spring fish were unimportant, and the small spring fish, although second in numerical importance, did not exceed 6·3 per cent. in either of the years under investigation. The relative proportion of each age group, by weight, is given in Table 3.

That the Ballisodare Fishery is a "grilse" fishery was suggested by the fact that the annual average weight of the fish taken over the period 1896 to 1939 has ranged from 4·17 lbs. in 1898 to 8·06 lbs. in 1929 (a year when the grilse runs in Ireland were very poor). A few summer fish were taken in April. In May they formed over 45 per cent. of the total catch, and for the remaining part of the season they formed the bulk of the catch, Table 4. The percentage of each age group in each month's catch is given in Table 2.

June was the best month for both grilse and previously spawned fish. We have the following sequence:—April, small spring fish with a few small summer fish, a few large spring fish, and a considerable proportion of previously spawned fish; May, small spring fish still the most important group, but almost equalled in number by the summer fish (1+ and 2+ winters); June, summer fish form 95 per cent. to 98 per cent. of the total, of which over 80 per cent. were grilse; and July, almost exclusively summer fish (grilse with about 4 per cent. to 5 per cent. of previously spawned fish). The percentage of the total of each age group in each month is given in Table 5.

Previously spawned fish comprised 6·4 per cent. and 5·5 per cent. of the catch in 1938 and 1939, respectively. None of these fish had more than one spawning mark on their scales. The greatest number of previously spawned fish occurred in the month of June, as will be seen from the estimated monthly catch of fish in the different age groups as indicated in Table 6. The scales of salmon of the Ballisodare River undergo considerable erosion, or more properly absorption, after a sojourn in fresh water. It is, therefore, quite impossible to make any estimate of the age when these fish entered the river as maiden fish. The number of scales from previously spawned fish examined in 1938 and 1939 was 39 and 30, respectively. Previously spawned fish can, however, be classified on "absence" (the period they spend in the sea between what would be, but for the intervention of man, two successive spawnings). In Table 7 the previously spawned fish from the catches of the two years have been so classified.

As might be expected in a river which produces mainly grilse, the "short absence" habit was the most prevalent.

Divided Migration and Return.

Table 8 gives the years in which the fish were hatched. It will be seen that the 1935 and 1936 year classes were the most important in 1938 and 1939, respectively. These year classes entered the river mainly as fish of 3+ years of age. This fact may also be seen from Tables 1 and 6.

Discussion of the early history of the fishery.

In a previous paper dealing with the early history of the Ballisodare Fishery (Went, 1940) it was suggested that the first smolt run in 1853 must have consisted of one-year smolts only. Fry derived from adult fish and eyed ova placed in the river in December, 1851, would not have to face such severe competition for food as their successors, when the river was more heavily stocked at a later period, and, therefore, it is quite possible that a considerably larger proportion of one-year smolts may have been produced than at the present time. Although the reports (Commissioners, 1858) do not make reference to a run of smolts in 1854, a fairly substantial run of fish in 1855 was noted, and from the average weight of 5 pounds it must be inferred that the majority of these were grilse. Incoming grilse in 1855 must have been derived from a run of smolts in 1854. These smolts must have been derived either from the six fish put above the Upper Falls at Ballisodare in 1852, or from the eyed ova or adult fish placed in the River Owenbeg in the previous year. The results of the

age determinations of the incoming populations in 1938 and 1939 show that either or both of the above possibilities may have accounted for the runs of fish in 1855.

The short life history of the salmon of this river as indicated was one of the factors which permitted the rapid development of this fishery. About 90 per cent. of the catches of each year under investigation were 3 + years old or less. Thus the period between the running of parents and their offspring will, on the average, be considerably less than 4 years. As mentioned previously, in the early stages of the fishery there were indications that the percentage of young fish might have been even greater than at present, in which case the "cycle" would have been shorter.

The survival of the fry derived from the three pairs of fish introduced from the River Moy, and from the small quantity of ova introduced in the same year, appears to have been quite exceptional; but it must be remembered that this was the first time in the history of the Owenbeg River that any salmon fry had been present. As is often the case when a species is introduced into areas where it was absent previously, the salmon fry must have thriven in order to populate the river system to such an extent as to transform barren waters into a prolific salmon fishery in such a short period.

Size Distribution.

Table 9 gives the estimated number of fish, occurring in each class interval of one inch, for the catches of the two years under investigation. Fish having lengths between 21⅞ and 27⅞ inches comprised 82·3 per cent. and 84 per cent. of the total catches in 1938 and 1939, respectively.

Average Sizes.

Monthly details of the average weights and lengths will be found in Table 10 (not reproduced), copies of which have been deposited in the Libraries of the Royal Dublin Society; Trinity College, Dublin; University College, Dublin; and the Department of Agriculture, Fisheries Branch, Dublin, from which the necessary details have been extracted.

(1) Grilse (1 + winters)—

	1938.		1939.	
Total number examined ...	483		357	
	lbs.	inches.	lbs.	inches.
Minimum	3¼	20¼	2¾	19
Average	6·43	24·60	6·44	24·61
Maximum	11¼	28¾	10¼	29·0

In 1938 the first grilse was taken on 20th May, and was 21¼ inches long, 4¼ lbs. weight, whilst in 1939 the first grilse was captured on 18th May, and was 23¾ inches long and weighed 5¼ lbs. The minimum weight and length were recorded on 15th July in 1938 and on 5th June in 1939. The largest fish was recorded in 1938 on 21st June and on 3rd July in 1939.

There was a slight increase in average size from May to July, as shown below :—

	1938.		1939.	
	lbs.	inches.	lbs.	inches.
May	4·8	23·7	5·75	24·3
June	6·42	24·6	6·37	24·45
July	6·44	24·6	6·58	24·90

It was estimated that in 1938 and 1939, respectively, 18·7 per cent. and 15·2 per cent. of the grilse were derived from one-year smolts, and 79·6 per cent. and 83·8 per cent. from two-year smolts; the remainder were derived from three-year smolts.

(2) Small spring fish (2 winters)—

	1938.		1939.	
Total number examined ...	34		65	
	lbs.	inches.	lbs.	inches.
Minimum	6	24½	6	24¼
			5¾	24½
Average	10·97	29·83	9·83	29·07
Maximum	16½	34½	19¼	35¼

In 1938 the fish of minimum weight and length was taken on 30th May. In 1939 the fish of minimum sizes (6 lbs. 24¼ inches and 5¾ lbs. 24½ inches) were taken on 14th April and 13th June, respectively.

The maximum size was recorded in 1938 on 3rd May and in 1939 on the 13th April.

It was estimated that 48·5 per cent. and 47·0 per cent. of the small spring fish in 1938 and 1939 were derived from one-year smolts, and 48·5 per cent. and 52·0 per cent. in the two years, respectively, were derived from two-year smolts; the remainder were derived from three-year smolts.

The two-year smolt class is, on the average, smaller than the one-year smolt class, as will be seen from the following table :—

	1938.		1939.	
Smolt age	1	2	1	2
Average weight in lbs. ...	11·5	10·42	10·04	9·92
Average length in inches ...	29·97	29·50	29·15	29·10

(3) Small summer fish (2 + winters)—

	1938.		1939.	
Total number examined ...	31		39	
	lbs.	inches.	lbs.	inches.
Minimum	7	26¼	7½	26½
			7½	26¼
Average	12·30	30·26	11·6	30·2
Maximum	19	35	15¼	32¾
			15¼	32¼
			15¼	32
			14	33

In 1938 the fish having minimum weight and length was recorded on the 25th May, whilst the heaviest fish was captured on 24th May. The minimum

weight was recorded in 1939 on two occasions, namely, on 15th and 18th May, but the latter was slightly longer than the former. The maximum weight of 15¼ lbs. was recorded on three occasions in 1939—30th May (32¾ inches), 5th June (32 inches), and 7th June (32¼ inches). A longer (33 inches) but considerably thinner fish weighing only 14 lbs. was taken on the 16th June. It was estimated that 53·5 per cent. and 40·8 per cent. of the small summer fish in 1938 and 1939, respectively, were derived from one-year smolts and the remainder from two-year and three-year smolts.

(4) Large spring fish (3 winters)—

Scales from only four specimens of this age group were examined, and the details are as follows. The four fish were taken in 1939 :—

Date of Capture.	*Weight in lbs.*	*Length in inches.*
3rd April, 1939	15½	33
11th April, 1939	21½	34¾
17th April, 1939	19¾	34¾
16th May, 1939	16	34

The first and last fish were derived from one-year smolts, and the other two from two-year smolts.

(5) Previously spawned fish (with S.M.'s)—

This age group consists of a heterogeneous group of fish having only one characteristic, namely, the presence of spawning marks on their scales. Average values are of little significance, and the most satisfactory method of classification is by (1) absence and (2) the age at first spawning. As mentioned previously, scales of salmon of the Ballisodare River undergo considerable erosion, so that determination of the age at first spawning is impossible, except in very few cases. In Table 11 the fish of this age group have been classified on their absence habit.

The following are the largest and smallest fish of this age group, examined for each year's catch :—

	1938.		1939.	
	lbs.	inches.	lbs.	inches.
Minimum size	6½	24¾	6	24
Maximum size	17¾	36	18¾	36½
	19½	35¼	17¾	36½

In 1938 the smallest fish was taken on 24th June, and exhibited the short absence habit. In 1939 the smallest fish was taken on 26th June, and also exhibited the short absence habit.

The maximum weight was recorded in 1938 on 12th May, and this fish exhibited the long absence habit. A longer but lighter fish exhibiting the long absence habit was taken on 11th April. In 1939 the greatest length, 36½ inches, was recorded on two occasions, namely, on the 24th April and 3rd May, but the fish caught in April was 1 lb. heavier than the fish caught later. Both these fish showed the long absence habit.

It might be mentioned here that, in Table 8 showing divided migration and return under the heading of previously spawned fish, an estimation of the age at first spawning was made from consideration of the size, scale readings, and absence habit.

Condition coefficient.

The condition coefficient (K) or the relationship between weight and length is determined according to the formula—

$$K = \frac{W}{L^3 \times 0{\cdot}00036}$$

where W = weight in lbs. and L = length in inches. This formula gives a figure approximating to unity for normally fed fish in Scottish rivers, for which the formula was devised (Menzies, 1921). Another method of expressing the relationship between weight and length is by the Condition Factor (C.F.) according to Corbett's scale, which is calculated by means of the formula:— C.F. = 100,000 W/L^3 where W = weight in lbs. and L = length in inches.

Many workers using British units prefer the latter formula. The relationship between the two values is evidently C.F. = $K \times 36$.

It might be mentioned at this stage that if a condition coefficient is calculated using the formula 100,000 W/L^3, where W = weight in kilogrammes, L = length in centimetres, the results will closely approximate to those obtained by using Menzies' formula given above.

Table 10 gives the average condition coefficients for the monthly catches in each age group. The mean values of the condition coefficient for all the fish investigated were 1·19 and 1·18, respectively, in the two years under investigation. The average condition coefficient used was calculated from the individual condition coefficients, and not from the average weights and lengths. Table 12, which has been extracted from Table 10, gives the average condition coefficients in the various age groups.

Apart from the large spring fish, which are too few to give reliable means, the spring fish are inferior to the summer fish in condition. This is the reverse of the condition found in the River Shannon (Went, 1938), but similar to the condition found in most investigations on Scottish salmon (Menzies and MacFarlane). The average condition coefficient of the grilse was the highest recorded for any river which has yet been adequately investigated. Similarly, the small summer fish were in exceptionally good condition; only the Rivers Spey, Tay, and Shannon of those investigated have average condition coefficients of the same order.

The monthly average condition coefficients have been extracted from Table 10 and are given in Table 13. In general, there is a rise in average monthly condition coefficients as the season progresses.

The grilse in the two years under investigation were divided into length groups of 2 inches, and the variations of the average condition coefficient are given in Table 14.

Erosion.

Erosion, or more correctly absorption, of the substance of the scales begins to take place when the gonads of the salmon are ripening. The so-called erosion usually takes place in fresh water, but it can also take place in the sea if the

fish have been delayed in reaching fresh water for any reason. All the scales examined were taken from fish captured in tidal water, and very few showed any signs of erosion. In 1938 none of the 591 sets of scales examined showed signs of erosion, but in 1939 12 out of a total of 499 were eroded to a certain extent. Both the small spring and summer fish showed considerable erosion in June, 1939 (50 per cent. of the small spring fish showed erosion, average erosion 1·7° on Menzies Scale, whilst for small summer fish the figures were 16 per cent. and 0·6°, respectively). The differences between the catches in the two years may have been due to the prevalent low water conditions in June, 1939, which delayed the ascent of fish.

Growth checks in the sea in 1937 and 1938.

Growth checks were observed in the scales of a considerable number of the small spring and summer fish. In the 1938 catch the checks were restricted in general to the growth made in 1937. Some of the small spring fish taken in 1939 showed checks in both sea years, but checks in the first sea year (1937) were more common. In a short article in the *Salmon and Trout Magazine* in 1939, the author mentioned that in Éire in 1938 a considerable number of diminutive small spring fish was observed in various rivers, and that some of the scales of these fish showed growth checks in the year 1937. The fact that checks were present in the centre of the growth region corresponding to the year 1937 in the scales of some small spring fish captured in 1939 in the Ballisodare Fishery, suggests that the conditions which caused such checks occurred towards the end of the summer of 1937. If a check in the growth of salmon in the sea in 1937 had occurred early in the spring no such signs could have occurred on the scales of small spring fish of 1939, since in the spring of 1937 they would only have just commenced the seaward migration as smolts.

Calculated lengths.

The length of each unspawned or "maiden" fish at the end of every year of its life was calculated in the usual way from measurements of the scales, i.e., assuming that the growth of the scale is strictly proportional to the growth of the fish.

A. *River Life.*

The relationships of the parr lengths are dealt with in this section. Preliminary investigation showed that, dealing with each year separately, the results for the two seasons in question were very similar, and, therefore, it is proposed to combine the observations for the two years to save unnecessary repetition.

In Table 15 the average growth in each smolt class is given. From this table it is obvious that the fastest growing smolts migrate first. The one-year smolts were the longest parr at the end of their first winter. Similarly, the two-year smolt class was on the average larger than the three-year smolt class at the same time.

A graphical illustration of the growth rate in the three smolt classes is afforded by Fig. 1A. The frequency distribution curves are given in Fig. 1B, in which the percentage frequency has been used to facilitate comparisons.

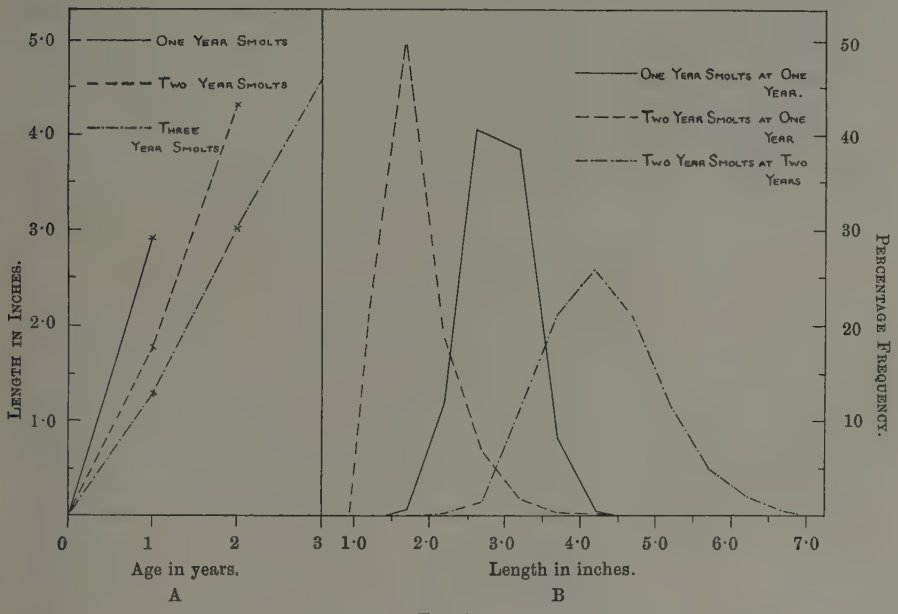

FIG. 1.

A. Growth curves of the different smolt classes.
B. Frequency distribution curves in the one and two year smolt classes at different periods.

In Table 16 the calculated lengths of parr in the different smolt classes are given for each age group.

In a previous publication dealing with the salmon of the River Shannon (Went, 1938) it was stated that fish of that river could be divided into two groups, depending on whether or not they showed freshwater growth in the spring prior to migration as smolts. For convenience those fish which showed little or no freshwater growth (new growth restricted to two new rings or less) were termed Type A smolts, and those showing a fairly large amount of growth were termed Type B smolts. Jones (1939), dealing with the Cheshire Dee, has now used other terms; the terms early and late migrants instead of the terms mentioned above. Unfortunately, these terms which are descriptive are not of general application, because it can be shown in many rivers that the so-called early and late migrants migrate together. Although Type A smolts of any smolt class will migrate as a class earlier than Type B smolts of the same smolt class, individually there is considerable intermingling. The terms the author has used previously have been retained in this paper.

Table 17 gives the percentage of each type of smolt occurring in each smolt age. In that table each year has been dealt with separately. As the results were of the same order in each year, the observations for both years have been combined in the following discussion.

The calculated lengths in inches of fish in the different groups are given in Table 18.

The growth curves of the two types in the one- and two-year smolt classes are illustrated graphically in Fig. 2A, and in Fig. 2B the frequency distribution curves of each type have been given. In the latter diagram the frequency distribution curves for the length of the two smolt types in the two-year smolt class at the end of the first winter have been added; percentage frequencies have been used for the sake of simplicity. Fig. 2B shows that in the two-year

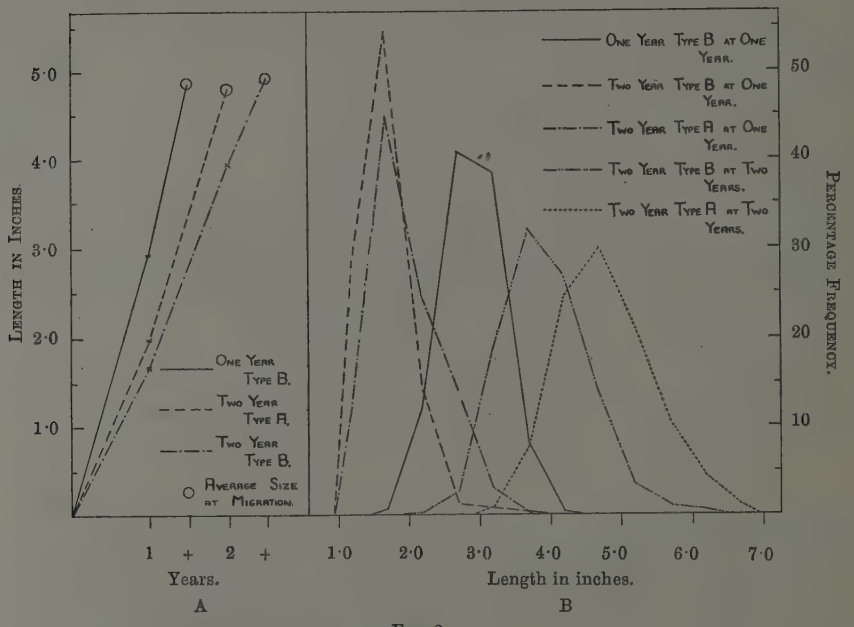

Fig. 2.

A. Growth curves of the more important growth types.

B. Frequency distribution curves of the various growth types at different periods of life.

smolt class Type A fish have, at the end of the second year in fresh water, a higher average length than the Type B fish of the same smolt class. It can be shown that the differences between the averages (means) in the two smolt types of the two-year smolt class are statistically significant[1]; that is to say, that if the number of observations were increased considerably the same effect would be observed, and the means would not approximate closely, one to the other.

[1] The differences measured in terms of their standard deviations equal 4·8.

Similarly, the means determined for the lengths of each smolt type in the two-year smolt class at the end of the first year can be shown to be statistically significant.[2]

A similar condition was observed in the River Shannon, and it was suggested that the parr must attain some physiological condition, associated, at least as an index, with a minimum size, before the smolt migration takes place. The results of the present investigation are not inconsistent with the view expressed with respect to the investigation of the River Shannon, but the minimum size which appears to operate is about 4·3 inches, instead of 5·5 inches for the River Shannon.

Assuming that the explanation given above is the correct one, at the end of the first year one should expect to find a definite sequence in average lengths in descending order as follows:—

One-year smolts Type A.
One-year smolts Type B.
{ Two-year smolts.
{ Three-year smolts.

It is not necessary that the sequence should extend to the two- and three-year smolts, but, as will be seen later, in actual fact such an extension was found. The first group of the above list, namely, the one-year smolts Type A, does not appear to be present in the Ballisodare River, but the other groups are present. At the end of the first year the sequence referred to above is as follows:

One-year	Type	B,	mean	length	2·92	inches.
Two	„	„	A,	„	„	1·96	„
Two	„	„	B,	„	„	1·66	„
Three	„	„	A,	„	„	1·50	„
Three	„	„	B,	„	„	1·20	„

Only small numbers of three-year smolts were observed, and as the average lengths cannot be considered significant they have been left out of the following discussion. At the end of the second year in the two-year smolt class we find that the Type A fish are longer than those of Type B, as follows:—

Type A fish, mean length 4·79 inches.
„ B „ „ „ 3·94 „

Usually speaking there is a clear-cut distinction on the scales of these salmon between growth made in fresh water and growth made in the sea. It is possible, therefore, to calculate for the Type B fish the size of the smolt. This calculation has been made for all the Type B smolts, and the results are given below, together with the mean lengths of the Type A smolts of the two-year smolt class:—

One-year	Type	B	smolts	...	4·86	inches	average	length.
Two „	„	A	„	...	4·79	„	„	„
Two „	„	B	„	...	4·92	„	„	„

[2] The differences measured in terms of their standard deviations equal 9·6.

The variation of the smolt size in the various groups shown above is small. It is noteworthy that the size of the smolts in the Ballisodare River is very much smaller than those of the River Liffey (Frost and Went, 1940) and of the River Shannon (Went, 1938).

In Table 16 the calculated lengths of every age group and smolt class have been given for the two years under investigation. Owing to the fact that there are so few individuals in all groups, except those containing the grilse derived from one- and two-year smolts, it is impossible to determine whether there is any differentiation in fresh water between the various age groups.

B. *Sea Life.*

The length at the end of every year in the sea was calculated for every fish with suitable scales. In Table 16 these lengths are given in the various age groups.

At the end of the first sea winter the grilse appear to have a greater average length than any other group. This is more clearly shown by comparing all grilse (for both years) with the remaining age groups, and the results of such a comparison are given below:—

Age Group.	*No.*	*Average length at end of 1st sea winter.*
Grilse	809	18·47 inches.
(2, 2+, & 3 age groups combined) ...	160	17·33 inches.

In the summer fish the increment made in the year of return to the river increases as the season progresses. This can be seen readily from Table 19. The increments made in 1939 were in every case slightly less than those made in 1938 in the same month.

C. *Correlation Tables.*

In this section it is proposed to discuss the relationship between the growth made in the various years of life, and for sake of convenience the data from both years under investigation have been combined.

(1) Correlation between parr lengths at the end of the first and second winters in the two-year smolt class.

Table 20 gives the correlation between the length of parr at the end of the first and second winter in the two-year smolt class. It is evident that the average increase in length during the second year was approximately 2·5 inches, no matter what the length was at the end of the first year.

A similar condition has already been described in the case of the River Shannon (Went, 1938).

(2) Correlation between smolt size and the length at the end of the first sea winter.

Previous mention was made of the fact that the grilse were, on the average, at the end of the first sea winter, longer than any other age group. In Table 21 grilse only have been considered, since no other homogeneous age group had sufficient individuals present to give accurate means.

It will be seen that if the smolts are grouped according to size, the length at the end of the first sea winter shows a gradual increase. The differences in the lengths at the end of the first sea winter are not proportional to the differences in the smolt lengths, so the average increment made in the sea in the first sea year becomes less as the smolt length increases.

(3) Correlation between lengths of grilse at the end of the first sea winter and at capture.

In Table 22 the fish have been grouped in one-inch class intervals for the length at the end of the first sea winter, and the mean length in inches at capture of each class interval has been determined.

If the figures are plotted in the form of a graph it will be obvious that the points lie close to a smooth curve. If the actual increment made in the summer of the return to the river is considered, it will be seen that the average increment is greater in those fish which have lengths at the end of the first sea winter between 16·95 and 18·95 inches. It might be expected, from the correlation given above, and from the fact shown earlier, that the average increment increases as the season progresses, that the proportion of fish whose length at the end of the first sea winter was between 16·95 and 18·95 inches would increase as the season progressed. In other words, it might be expected that, speaking generally, in the beginning of the season the size of the incoming populations of grilse would show the biggest range in length, and as the season progressed the lengths would become more uniform. This was actually found to be the case.

RÉSUMÉ.

1. Material, consisting of sets of scales and data, was collected from the Ballisodare Net Fishery in 1938 and 1939. The data obtained have been subjected to arithmetical manipulation in order to get a true idea of the stocks of salmon of this river.

2. The bulk of the salmon migrated as one and two year smolts, and the percentage of one year smolts was comparatively high (about 20 per cent.).

3. Grilse formed just over 80 per cent. of the total; small spring and summer fish and previously spawned fish making up the remainder in almost equal proportions. About 66 per cent. of the annual catch were taken in the month of June and nearly 30 per cent. in the month of July. The majority of the previously spawned fish showed the short absence habit.

4. The early history of the fishery was discussed in the light of the age determinations.

5. Grilse of the Ballisodare River are on the average heavy fish. The small summer fish are over a pound heavier than the small spring fish.

6. The average condition coefficient of the grilse was the highest yet recorded for any river adequately investigated, and the small summer fish were in very good condition.

7. Checks were observed in the scales of salmon taken in the two years under investigation corresponding to the middle of the period of growth for the 1937 season.

8. The lengths of all maiden fish at the end of every year of life were calculated from scale measurements. The faster growing parr migrated first, Fig. 1. Some fish showed on their scales growth in fresh water in the spring prior to migration as a smolt (Type B smolts), whereas others showed little or no growth before migration (Type A smolts). Type B smolts at the end of every year of life were smaller on the average than Type A smolts of the same smolt class at the same time, Fig. 2. The differences in the calculated lengths can be shown to be statistically significant. The results led to the suggestion that the parr must attain some physiological condition associated, at least as an index, with a minimum size before the smolt migration takes place. This minimum size appears to be about 4·3 inches.

Grilse had a greater length at the end of the first sea winter than any other age group. In the summer fish the increment made in the year of return to the river increased as the season progressed.

The relationship in the two year smolt class between the lengths at the end of the first winter, L_1, and the second winter, L_2, was found to be $L_2 = L_1 + 2{\cdot}5$.

In the grilse there appears to be a close relationship between (1) the smolt length and the length at the end of the first sea winter, and (2) the length at the end of the first sea winter and the length at capture. The increment made in the second summer in the grilse was greatest in those fish which had, at the end of the first sea winter, lengths between 16·95 and 18·95 inches.

Additional Note on the History of the Ballisodare Fishery.

Since the compilation of the report on the history of this fishery my notice has been drawn to a reference in Part II of the Tenth Annual Report of the Fishery Board for Scotland (1892) on the subject of the Ballisodare hatchery. The Inspector of Salmon Fisheries for Scotland noted that in 1891 he was informed that salmon ova from the Rhine had been obtained by the proprietor of the Ballisodare fishery, with a view to increasing the size of the salmon, and as a consequence there had been a considerable increase in the average weight of the fish captured.

On page 304 of the report on the history of this fishery (Went, 1940) reference was made to the fact that the average weight of the fish had increased in each decade from the beginning of the century. It is not possible to state whether the distribution of fry derived from Rhine fish was responsible for the increase in size already noted, but the facts are given for what they are worth.

Acknowledgments.

I should like to take this opportunity of expressing my thanks to Mr. F. F. Scott, Manager of the Ballisodare Fishery, for collecting the sets of scales and data. I am also indebted to Mr. G. P. Farran, B.A., Chief Inspector of Fisheries, Department of Agriculture, Fisheries Branch, Dublin, for the interest he has shown in the work, and to Mr. P. J. Roche, M.SC., for his kindness in reading through the MS.

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APPENDIX.

TABLE 1.

Percentage of each smolt age in each age group.

Smolt Age	Age Group					Total (Maiden Fish)
	1+	2	2+	3	With SM's	
1938						
One Year	18.7	48.5	53.5	-	21.3	22.9
Two Years	79.6	48.5	42.8	-	78.7	75.2
Three Years	1.7	3.0	3.7	-	-	1.9
Total	100.0	100.0	100.0	-	100.0	100.0
1939						
One Year	15.2	47.0	40.8	50.0	47.4	18.8
Two Years	83.8	52.0	59.2	50.0	48.5	80.3
Three Years	1.0	1.0	-	-	4.1	0.9
Total	100.0	100.0	100.0	100.0	100.0	100.0

TABLE 2.

Percentage of each age group in the catch of each month

Month	Age Group						Total
	1+	2	2+	3	with SM's		
					Spring Fish	Summer Fish	
1938							
March	-	60.0	-	-	40.0	-	100
April	-	70.4	-	-	29.6	-	100
May	7.1	41.8	41.8	-	9.3	-	100
June	89.4	0.8	3.4	-	-	6.4	100
July	95.5	0.6	0.6		-	3.3	100
Total	81 3	6.3	6.0	-	1.6	4.8	100
1939							
April	-	65.0	10.0	7.5	17 5		100
May	15.1	49.0	30.3	1.9	3 8	-	100
June	83.8	4.7	6.4	-	0 3	4.8	100
July	94.6	-	-	-		5.4	100
Total	82.6	6.3	5.4	0.2	0.8	4 7	100

TABLE 3.

Percentage composition of the catches in 1938 and 1939 by weight.

Winters in Sea	1938				1939				
	1+	2	2+	With SM's	1+	2	2+	3	With SM's
% of total catch by weight	70.4	9.3	10.0	10.3	74.2	8.7	8.8	0.5	7.8

TABLE 4.

Percentage of Spring and Summer Fish in each month's catch.

Month	1938		1939	
	Spring Fish	Summer Fish	Spring Fish	Summer Fish
March	100%	-	-	-
April	100%	-	90.0%	10.0%
May	51.2%	48.8%	54.6%	45.4%
June	0.8%	99.2%	5.0%	95.0%
July	0.6%	99.4%	-	100.0%
Total	7.9%	92.1%	7.3%	92.7%

TABLE 5.

Percentage of the total of each age group in each month.

Month	Age Group					Total
	1+	2	2+	3	With SM's	
1938						
March	-	4.5	-	-	3.0	0.5
April	-	25.2	-	-	10.3	2.4
May	0.7	59.7	62.7	-	12.8	9.0
June	66.8	8.1	34.6	-	59.6	60.6
July	32.5	2.5	2.7	-	14.3	27.5
Total	100.0	100.0	100.0	-	100.0	100.0
1939						
April	-	25.3	4.5	73.4	7.9	2.5
May	0.6	26.9	19.4	26.6	2.4	3.5
June	65.4	47.8	76.1	-	59.4	64.3
July	34.0	-	-	-	30.3	29.7
Total	100.0	100.0	100.0	100.0	100.0	100.0

TABLE 6.

Estimated monthly catch of fish in different age groups.

Month	Age Group					Total
	1+	2	2+	3	With SM's	
1938						
March	-	9	-	-	6	15
April	-	50	-	-	21	71
May	20	118	118	-	26	282
June	1705	16	65	-	121	1907
July	830	5	5	-	29	869
Total	2555	198	188	-	203	3144[x]
1939						
April	-	98	15	11	26	150
May	32	104	64	4	8	212
June	3282	185	251	-	198	3916
July	1711	-	-	-	101	1812
Total	5025	387	330	15	333	6090[xx]

x 7 fish unaccounted for xx 17 fish unaccounted for

TABLE 7.

Showing divided migration and return. The table gives the years in which the fish examined were hatched as percentages of the total for each year.

Returned in 1938 as	Hatched in the year					Total
	1932	1933	1934	1935	1936	
Grilse	-	-	1.4	64.7	15.2	81.3
Small Spring Fish	-	0.2	3.0	3.1	-	6.3
Small Summer Fish	-	0.2	2.6	3.2	-	6.0
Previously Spawned[x]	2.1	0.4	2.5	1.4	-	6.4
Total	2.1	0.8	9.5	72.4	15.2	100.0

Returned in 1939 as	Hatched in the year					Total
	1933	1934	1935	1936	1937	
Grilse	-	-	0.7	69.2	12.7	82.6
Small Spring Fish	-	0.1	3.3	2.9	-	6.3
Small Summer Fish	-	-	3.2	2.2	-	5.4
Large Spring Fish	-	0.1	0.1	-	-	0.2
Previously Spawned[x]	0.2	1.1	2.3	1.9	-	5.5
Total	0.2	1.3	9.6	76.2	12.7	100.0

x Approximate values

TABLE 8.

"Absence habit" of previously spawned fish.

Absence	1938		1939		Both years	
	No.	%	No.	%	No	%
Short (less than one year)	145	71.5	273	82.0	418	78.1
Long (a full year)	53	26.1	47	14.1	100	18.7
Very long (more than a full year)	5	2.4	13	3.9	18	3.2

TABLE 9.

Calculated frequency distribution of lengths in different age groups for the catches of the years 1938 and 1939.

Size in inches	1938					1939				
	Age Group				All Fish	Age Group				All Fish
	1+	2	2+	With SM's		1+	2	2+	With SM's	
19	-	-	-	-	-	13	-	-	-	13
20	16	-	-	-	16	-	-	-	-	-
21	62	-	-	-	62	170	-	-	-	170
22	192	-	-	-	192	390	-	-	-	390
23	609	-	-	-	609	838	-	-	-	838
24	657	7	-	6	670	1511	18	-	13	1542
25	596	5	-	11	612	1255	14	8	26	1295
26	320	-	7	38	365	637	12	14	43	700
27	88	-	17	38	143	177	43	22	104	338
28	15	23	19	22	79	-	59	59	67	148
29	-	78	36	5	119	34	93	150	4	190
30	-	26	47	-	73	-	81	55	4	235
31	-	48	13	5	66	-	51	22	13	119
32	-	-	30	23	53	-	4	-	30	56
33	-	4	5	14	23	-	4	-	4	12
34	-	7	7	12	26	-	4	-	17	32
35	-	-	7	25	32	-	4	-	-	4
36	-	-	-	4	4	-	-	-	8	8
Total	2555	198	188	203	314x	5025	387	330	333	6090xx

Including: 4 large spring fish and 11 large spring fish.
x 7 fish unaccounted for. xx 17 fish unaccounted for.

TABLE 11

Average weights of previously spawned fish classified on "absence".

Absence	1938			1939		
	No.	lbs.	inches	No.	lbs.	inches
Short	27	9.4	28.8	19	8.67	27.5
Long	11	15.95	34.1	10	12.5	32.0
Very Long	1	13.75	32.5	1	13.75	32.75

TABLE 12.

Average Condition Coefficients (K) and Condition Factors (according to Corbett's scale) (C.F.) of the different age groups.

Age Group	1938		1939	
	K.	C.F.	K.	C.F.
1+	1.20	43.2	1.19	42.8
2	1.12	40.3	1.12	40.3
2+	1.16	41.7	1.16	41.7
3	-	-	1.24	44.5
With SM's	1.14	41.0	1.14	41.0
Total	1.19	42.8	1.18	42.4

TABLE 13.

Average monthly Condition Coefficients and Condition Factors

Month	1938		1939	
	K.	C.F.	K.	C.F.
March	1.12	40.3	-	-
April	1.10	39.6	1.15	41.4
May	1.15	41.4	1.11	40.0
June	1.20	43.2	1.19	42.8
July	1.20	43.2	1.20	43.2

TABLE 14.

Condition Coefficients in the various class intervals of grilse.

Class interval in inches	1938 Grilse (1+ winters)	1939 Grilse (1+ winters)
18	-	1.12 (1)
20	1.16 (15)	1.20 (12)
22	1.18 (149)	1.17 (91)
24	1.20 (235)	1.17 (192)
26	1.20 (77)	1.20 (59)
28	1.32 (3)	1.14 (2)

The numbers in brackets indicate the number of fish observed

TABLE 15.

Calculated growth in fresh water in the different smolt classes.

Smolt Age	No	Average length in inches at end of			Average smolt length in inches
		1st year	2nd year	3rd year	
1	219	2.92	-	-	4.86
2	725	1.79	4.32	-	4.86
3	10	1.3	3.0	4.6	5.00

TABLE 16.

Calculated average length in inches at end of each winter of River and Sea Life.

Group	No. of Fish	River Life			Sea Life		
		1	2	3	1	2	3
1938							
1.1+	88	2.89	-	-	18.05	-	-
2.1+	373	1.80	4.28	-	18.40	-	-
3.1+	8	1.24	2.86	4.50	18.95	-	-
1.2	17	2.85	-	-	16.70	29.97	-
2.2	17	1.93	4.6	-	18.03	29.50	-
3.2	1	2.0	4.2	6.2	19.3	31.00	-
1.2+	12	2.7	-	-	17.2	28.6	-
2.2+	11	2.1	4.6	-	16.6	28.3	-
3.2+	1	1.1	2.7	4.5	18.1	28.5	-
1939							
1.1+	54	2.97	-	-	17.94	-	-
2.1+	283	1.78	4.32	-	18.75	-	-
3.1+	3	1.43	3.17	4.87	18.8	-	-
1.2	29	3.03	-	-	17.18	29.45	-
2.2	33	1.89	4.03	-	17.94	28.27	-
3.2	1	1.4	2.7	4.6	16.6	28.0	-
1.2+	16	2.9	-	-	16.8	27.5	-
2.2+	18	2.00	4.46	-	17.5	28.3	-
1.3	2	3.5	-	-	18.9	28.8	33.5
2.3	2	2.2	4.3	-	19.0	28.2	34.8

TABLE 17.

Estimated proportion of the different smolt types in each smolt class for maiden fish.

Smolt Age	1938		1939	
	Type A Smolts	Type B Smolts	Type A Smolts	Type B Smolts
1 year	-	22.9%	-	18.8%
2 years	32.7%	42.5%	41.6%	38.7%
3 years	0.8%	1.1%	0.6%	0.3%
Total	33.5%	66.5%	42.2%	57.8%

TABLE 18.

Calculated lengths for the different smolt types in the one and two year smolt classes.

Smolt Class	Growth Type					
	A			B		
	Length at end of		Length of smolts	Length at end of		Length of smolts
	1 year	2 years		1 year	2 years	
One year	-	-	-	2.92	-	4.86
Two year	1.96	4.79	4.79	1.66	3.94	4.92

TABLE 19.

Average growth increment (I) in inches made in final summer in the grilse and small summer fish.

Month	1938				1939			
	1+ Winters		2+ Winters		1+ Winters		2+ Winters	
	No.	I	No.	I	No.	I	No.	I
April	-	-	-	-	-	-	4	1.3
May	3	5.6	13	2.0	10	4.77	15	1.8
June	301	6.22	11	2.8	240	5.65	16	2.4
July	165	6.40	-	-	100	6.13	-	-

TABLE 20.

Correlation between lengths at the ends of first winter (L_1) and second winter (L_2) in fresh water for the two year smolt class.

Length at end of 1st winter in inches L_1	No.	Average length at end of second winter in inches L_2	Average increment made in second season in inches
0.95-1.45	170	3.73	2.53
1.45-1.95	369	4.18	2.48
1.95-2.45	144	4.67	2.47
2.45-2.95	51	5.23	2.53
2.95-3.45	20	5.70	2.50
3.45-3.95	1	6.1	2.4

TABLE 21.

Correlation between smolt length and length at the end of the first sea winter for the grilse.

Smolt size in inches	No. of individuals	Mean length in inches at end of 1st sea winter	Mean increment in inches
3.0-3.4	5	17.5	14.3
3.5-3.9	38	18.0	14.3
4.0-4.4	189	18.1	13.9
4.5-4.9	260	18.5	13.8
5.0-5.4	193	18.9	13.7
5.5-5.9	83	19.0	13.3
6.0-6.4	28	19.2	13.0
6.5-6.9	7	19.7	13.0

TABLE 22.

Correlation between lengths of the grilse at the end of the first sea winter and at capture.

Length at end of 1st Sea Winter	Mean length at capture	Mean Increment	Number of Individuals
14-14.9	19.0	4.6	1
15-15.9	20.8	5.3	7
16-16.9	22.2	5.8	64
17-17.9	23.6	6.2	191
18-18.9	24.6	6.2	234
19-19.9	25.5	6.0	195
20-20.9	26.0	5.6	81
21-21.9	26.2	4.7	21
22-22.9	26.8	4.4	6

No. 36.

THE EVOLUTION OF THE ATMOSPHERE.

By J. H. J. POOLE, Sc.D.

[Read January 28. Published separately February 24, 1941.]

The origin of our present atmosphere is a problem which received a fair amount of attention from Lord Kelvin and others (1) about the beginning of the present century. The general conclusion arrived at was that the primitive atmosphere was unlikely to have contained any free oxygen, and consisted of a mixture of CO_2, water vapour, and nitrogen. F. W. Clarke gives an interesting résumé of these views in "The Data of Geochemistry" (5th edition) (2), and points out some of the difficulties that arise when the known chemical data of the lithosphere are applied to the problem. Jeffreys (3) has also dealt with the subject in his book, "The Earth." He lays stress on the difficulty of explaining the formation of free oxygen from such an atmosphere. It is well known that the chlorophyl of green plants is capable of liberating oxygen from CO_2 under the action of light, but such plants respire CO_2, using up oxygen, when photosynthesis is not occurring. He concludes that for any form of life to start free oxygen is necessary. To explain our present atmosphere we should, therefore, have to assume that the primitive atmosphere contained at least some free oxygen, but, as will be seen later, the large excess of free carbon in the lithosphere renders this highly improbable. It is perhaps advisable at this stage to state that what is meant in this paper by the primitive atmosphere is the atmosphere present after the formation of the ocean.

Sir James Jeans (4) has also dealt with the possible loss of the lighter constituents of a planetary atmosphere by their escape from the gravitational field of the planet. He shows that the earth will be able to retain all gases except hydrogen and possibly helium, and that, unless the temperature of the outer atmosphere is above about 520° K., the rate of escape of even hydrogen will be excessively slow and of little cosmical importance. In the theory of the evolution of the atmosphere which I advance in this paper the escape of hydrogen into space is, however, one of the governing factors. A realisation of its importance is due to recent advances in our knowledge of the structure of the atmosphere derived from free or manned balloon ascents, the transmission of sound at moderately high levels, and, more especially as regards the higher levels, from the reflection of radio waves.

It is perhaps permissible at this point to indicate briefly the present views on the temperature and condition of the atmosphere at various heights. The atmosphere may be divided roughly into three regions—i.e., the troposphere,

the stratosphere, and the ionosphere. The troposphere reaches to a height of about 10 km., and is approximately in convective equilibrium, the temperature falling with height at a rate of about 5° C. per km. till the tropopause is reached. The temperature at this height is the lowest terrestrial temperature, about 220° K. The stratosphere may be taken as extending from the tropopause at about 10 km. to the bottom of the ionosphere at about 100 km. In this layer the temperature probably rises again with height. It is generally held that convective mixing of the atmosphere in the stratosphere is small, if it occurs at all. There is an appreciable quantity of ozone in the stratosphere, and the ozone is responsible for the sharp cut-off of the sun's spectrum at about 2900 A. It may be noted that light of shorter wave length than this seems to be lethal to most forms of life. This is another argument for the view that oxygen would be required for the start of life, at least in its terrestrial form. CO_2 could not produce this effect, as it does not absorb in this region of the spectrum.

The ionosphere commences at a height of about 100 km., and extends to the limits of the terrestrial atmosphere. In this layer intense ionisation is produced by solar radiation, probably mostly in the form of short ultra-violet light; although some of it may be due to corpuscular radiation. The degree of ionisation depends on the height, showing roughly two main maxima, one at about 100 km., generally known as the Kennelly Heaviside Layer, and the second at about 300 km., the Appleton layer or F region. The heights of these layers are variable, depending on the time of day. The concentration of ions per c.c. is greatest in the F layer, being of the order of 10^5 electrons per c.c. The temperature of the F layer appears at first sight to be surprisingly high, probably at least 1000° K. It will be seen later that at this temperature any hydrogen or helium present in the layer would rapidly escape into space. This agrees with the fact that hydrogen is apparently absent from the upper atmosphere, and also that the amount of helium present in the whole atmosphere is considerably less than the amount that must have been liberated from the rocks during geological time by the decay of their radioactive constituents, the deficiency presumably having escaped into space. We may take it, therefore, that even at the present time the earth is unable to retain hydrogen. For fuller particulars of our present knowledge of the atmosphere, articles by E. V. Appleton (5), in the "Report on Progress in Physics," **2**, 1935. on the Radio exploration of the upper atmospheric ionisation, and by S. Chapman and W. C. Price (6), in **3**, 1936, of the same journal, on the Upper Atmosphere may be consulted.

The short wave ultra-violet which produces ionisation in the ionosphere will probably also produce chemical dissociation of the molecules present. If only elementary molecules such as H_2, O_2, or N_2, are present this effect will not have any effect on the average chemical composition of the atmosphere, except that it will accelerate the loss of hydrogen, a hydrogen atom at any temperature possessing $\sqrt{2}$ times the velocity of a hydrogen molecule at the same temperature. If, however, H_2O or any compound of hydrogen is present and is dissociated,

the chemical nature of the atmosphere will gradually change. Thus if water dissociates into hydrogen and oxygen, some of the hydrogen will escape, and we will be left with an excess of free oxygen, which, owing to its greater molecular weight, will tend to move from the upper to the lower layers, thus leading to a slow accumulation of free oxygen in an atmosphere which originally contained oxygen only in the form of H_2O. We thus have a plausible explanation of how the primitive atmosphere, which originally contained no free oxygen, might in the course of time develop enough free oxygen to enable plant life to start and liberate much larger quantities of oxygen by the photosynthetic decomposition of CO_2, thus finally leading to our present atmosphere. It might be suggested that CO_2 itself might yield oxygen by dissociation under ultra-violet light. For two reasons this effect is probably not important. Any dissociation phenomena will probably be a reversible action, and unless one of the products of decomposition is removed a steady state will be attained. This does not occur in the case of a hydrogen compound since the hydrogen produced slowly escapes. Neither oxygen nor carbon will, however, escape, and any separation of the dissociated products would be produced by one of them diffusing faster downwards out of the dissociation layer; as might occur from the difference in their molecular weights. It is possible indeed that this method of separation would be as efficient as the escape of hydrogen into space, but the CO_2 is also handicapped by its high molecular weight. In any mixed atmosphere the relative concentration of the lighter constituents will be much greater in the upper layers of the ionosphere. Thus in an atmosphere of CO_2, N_2, and H_2O, of respective molecular weights 44, 28, and 18, we would expect the outer layers to be very largely N_2, and H_2O, with very little CO_2. The amount of H_2O will depend on the temperature at the tropopause, but in any case the amount of CO_2 at the level of active dissociation would be small, the outer nitrogen layer thus absorbing all the active ultra-violet before much CO_2 could be dissociated. Moreover, this effect does not interfere with the general conclusion that the original birth of free oxygen in the atmosphere is due to ultra-violet light from the sun. In the sequel I have attempted to examine this thesis more minutely, and as so many chemical and physical considerations enter into even a very incomplete discussion of the problem, I have divided the paper under various headings.

A.—Constitution of Primitive Atmosphere.

The mass of the present atmosphere is about $5{\cdot}2 \times 10^{15}$ tonnes, of which oxygen accounts for $1{\cdot}2 \times 10^{15}$ tonnes. This oxygen has presumably mostly been derived from the CO_2 in the primitive atmosphere and a corresponding amount of free carbon should be present in the lithosphere. F. W. Clarke (*loc. cit.*) takes the lithosphere as the outer shell of the earth to a depth of 10

miles, and as the data given here are mostly derived from his figures, the same definition of the lithosphere is taken.

It must be remembered, however, that during the denudation of an igneous rock oxygen is removed from the atmosphere by the oxidation of ferrous oxide to ferric oxide. During this process, also, about 65% of the sodium in the originally igneous rock is transferred to the ocean. Since the percentage of sodium in the average igneous rock and the total quantity of sodium in the ocean are known, we can estimate the total mass of the igneous rocks denuded during the course of geological time, and hence the mass of the sedimentary rocks in the lithosphere. These deposits can be roughly divided into shales, sandstones, and limestones, their respective abundance being 80, 15, and 5% of the total sedimentary rocks. Taking Clarke's figures we obtain the following values :—

Mass of shales $= 7{\cdot}9 \times 10^{17}$ tonnes.
Mass of sandstones $= 1{\cdot}48 \times 10^{17}$ tonnes.
Mass of limestones $= 0{\cdot}47 \times 10^{17}$ tonnes.

These figures are naturally rather uncertain, but the uncertainty probably does not exceed a factor of two. This method of obtaining the mass of the sedimentary rocks was originally worked out by Joly (7) in 1899, but I have followed the later estimates made by Clarke.

We are now able to form an estimate of the oxygen used up in the formation of the sedimentary rocks. I have taken the iron/oxygen ratio in the average igneous and sedimentary rock, and then, assuming that all the iron contained in the known mass of igneous rocks denuded has been oxidized to an extent corresponding to these two ratios, I find that a mass of oxygen of $1{\cdot}3 \times 10^{15}$ tonnes has been lost from the atmosphere by this action. This figure agrees reasonably well with a previous estimate, made by C. H. Smyth (8), of 69% of the present amount of oxygen, i.e. $0{\cdot}84 \times 10^{15}$ tonnes. Since it appears later that we are faced with a deficiency of oxygen in the present atmosphere when the buried free carbon is calculated, I have taken my own estimate as being the larger. We thus arrive at a total figure of $2{\cdot}5 \times 10^{15}$ tonnes as the total amount of oxygen liberated by reduction of the CO_2 in the primitive atmosphere. The mass of this CO_2 would be $3{\cdot}4 \times 10^{15}$ tonnes, containing 9×10^{14} tonnes carbon.

To this figure we must add the amount of CO_2 which has apparently been removed from the atmosphere during the formation of the sedimentary rocks. The relevant data are given in Table 1 :—

TABLE 1.

Rock.	Mass in tonnes.	Percentage CO_2.	CO_2 Content in tonnes.
Igneous ...	$9{\cdot}85 \times 10^{17}$	0·1	$9{\cdot}85 \times 10^{14}$
Shale ...	$7{\cdot}9 \times 10^{17}$	2·63	$2{\cdot}08 \times 10^{16}$
Sandstone ...	$1{\cdot}48 \times 10^{17}$	5·03	$0{\cdot}74 \times 10^{16}$
Limestone ...	$0{\cdot}47 \times 10^{17}$	41·54	$1{\cdot}95 \times 10^{16}$

From this it will be seen that the total amount of CO_2 in the sedimentary rocks is $4{\cdot}77 \times 10^{16}$ tonnes, whereas the parent igneous rocks would only supply $0{\cdot}1 \times 10^{16}$ tonnes, leaving say $4{\cdot}7 \times 10^{16}$ tonnes to be derived from the primitive atmosphere or some other unspecified source. It may be noticed that the limestones contain nearly 41% of the total CO_2 in the sediments. This CO_2 has presumably been extracted from the ocean, and hence ultimately from the atmosphere.

The next question to be considered is the amount of free carbon present in the lithosphere. The coal reserves of the world are estimated to be about 7×10^{12} tonnes (9). To this should be added the petroleum deposits, for which no very reliable data can be given; but, as will be seen, neither of them accounts for any important part of the free carbon content of the lithosphere. The only major constituent of the lithosphere which contains free carbon is shale, according to Clarke. An average shale contains 0·8% free carbon, which is presumably of organic origin, and hence must at some time have been present as CO_2 in the atmosphere. This amount of free carbon is very large, being $6{\cdot}3 \times 10^{15}$ tonnes. We have seen, however, that the free oxygen, which is at present in the atmosphere or has been removed from the atmosphere during the oxidation of the sediments, accounts for only 9×10^{14} tonnes of carbon, which leaves a balance of $5{\cdot}4 \times 10^{15}$ tonnes unaccounted for. It seems improbable that this carbon was ever present at one time as CO_2 in the atmosphere, for if this were the case we would have a balance of $1{\cdot}4 \times 10^{16}$ tonnes of oxygen subsequently lost from the atmosphere. It seems unlikely that oxygen could escape from the atmosphere in any large quantity. To explain its disappearance we might assume that the primeval crust of the earth was less fully oxidized than the present crust, and had, during geological time, taken up large quantities of oxygen. There is, however, a grave objection to this view. We have seen that the liberation of oxygen in the atmosphere is mainly due to plant life. In Archaean times it seems highly probable that there was no plant life, and, therefore, presumably very little oxygen in the atmosphere. An igneous rock of Archaean age should, therefore, be poorer in oxygen than igneous rocks of later ages, and such an effect has, as far as I am aware, not been observed. The mass of the primeval atmosphere would also have been very large.

If we reject this hypothesis, we seem to be left with two alternatives. The original crust may have contained the excess carbon in a form in which it could be slowly oxidized to CO_2 in the atmosphere, and then go through the organic cycle which led to its present concentration in the shales. The facts that volcanoes evolve CO_2, and that graphite deposits, of apparently non-organic origin, are found to a small extent in Archaean regions, lend a certain amount of support to this view. It would involve, however, the assumption that the original igneous rocks of the lithosphere were appreciably different in carbon content from the existing igneous rocks. The theory is also open to the same objection, that the process of gradual oxidation could not commence till plant life had started. As it is a cyclic change, carbon being simply removed slowly

from the igneous rocks to the shales, it will lead to no difficulties in the oxygen balance. Again, however, I am unaware that there is any evidence that Archaean igneous rocks contain on the average more free carbon than later types. It seems highly improbable that an igneous rock after solidification could undergo bulk oxidation with the evolution of the resulting CO_2. It is known, for instance, that helium, a much more mobile gas, is very largely retained in such rocks (10).

The other alternative is that the excess carbon was present in the primitive atmosphere as a compound gas other than CO_2. The most probable gas would be methane, CH_4. The earth seems to be relatively poor in hydrogen compared with its presumable parent the sun. This is usually attributed to the rapid loss into space of hydrogen during the very early stages of the earth's history. The major planets, however, managed to retain most of their hydrogen, and it has recently been found that their atmospheres consist largely of methane. The earth apparently was able to retain water vapour, and hence should also have retained CH_4, the density of which is only slightly less than that of water vapour. It might be reasonable, therefore, to conclude that CH_4 was present in the primitive atmosphere, but its subsequent disappearance with the evolution of free carbon in the shales is not easily explained. Methane is chemically rather inactive, and not actively poisonous to vegetable life. It is inflammable, its full oxidation producing CO_2 and H_2O. It is possible that CH_4 in the upper atmosphere might dissociate under the action of ultra-violet light giving carbon and hydrogen, which would subsequently escape, leaving an increasing balance of free carbon. It seems difficult to imagine, however, that this carbon could have been deposited as a solid layer on the early surface of the earth, besides the quantity of CH_4 to be broken up would have been very large, and presumably the escape of the large quantity of hydrogen involved would have taken a considerable time even on the geological time scale. Thus, even if free oxygen could be present in the atmosphere when free carbon was being produced in the upper atmosphere, an assumption which involves certain chemical difficulties, as the two elements would nearly certainly combine under the stimulus of ultra-violet light to form either CO or more probably CO_2, it seems plain that for a considerable period the atmosphere would have continued to contain large quantities of CH_4.

We might, it is true, imagine that the first stage of the evolution of the atmosphere was the oxidation of CH_4 to CO_2, produced by the photo-dissociation of CH_4 and H_2O, and the gradual escape of the hydrogen. This mechanism will lead again to the difficulty of explaining the oxygen deficiency, as it would lead to a state in which nearly all the carbon in the lithosphere was present as CO_2 in the atmosphere, since plant life could not start to remove the carbon till free oxygen was present. Granting, however, that enough of the free oxygen produced by the photo-dissociation of H_2O could have accumulated, in an atmosphere containing large quantities of CH_4, to render plant life possible, a cyclic process can be envisaged, in which plant life removes carbon from the

atmosphere, liberating more free oxygen. This oxygen would under the action of ultra-violet light produce more CO_2 from the CH_4, leading finally to the complete removal of the CH_4, and the concentration of the resulting carbon in the lithosphere.

It is not claimed that this is a satisfactory explanation, in fact no good explanation of the excess of carbon in the lithosphere has yet been put forward. To arrive at a rough idea of the constitution of the primitive atmosphere, I have assumed that the excess carbon was present as methane. If this view is rejected, we must conclude that the carbon was present in the original lithosphere, and has subsequently been slowly oxidized, then passing through the plant life cycle. The change involved in the proposed constitution would only be the removal of the CH_4. It may be remarked that, as shown later, a primitive atmosphere containing no methane is favoured by the physical evidence.

The proposed composition of the primeval atmosphere, neglecting the rarer constituents, such as argon, etc., and water vapour, of which it would be impossible to calculate the mass unless precise data of temperature distribution and degree of saturation at various heights were assumed, is given in Table 2. The mass of CH_4 is calculated on the view that it accounts for all the excess carbon. The CO_2 content has been divided into two parts: (*a*) CO_2 required to furnish the oxygen at present in the atmosphere or subsequently removed by the oxidation of the sediments, and (*b*) CO_2 used up in the formation of the sediments. The figure arrived at for the total mass of the primitive atmosphere is a maximum estimate, as it neglects the CO_2 evolved from the lithosphere during geological time due to volcanic activity. This may amount to a very considerable quantity, with a corresponding reduction in the mass of the primitive atmosphere.

TABLE 2.

	Mass in tonnes.	Mass of Carbon subsequently liberated.
CO_2 (*a*) Required to supply Oxygen ...	$0{\cdot}34 \times 10^{16}$	$0{\cdot}9 \times 10^{15}$
(*b*) Absorbed by sediments	$4{\cdot}7 \times 10^{16}$	Nil.
CH_4	$0{\cdot}72 \times 10^{16}$	$5{\cdot}4 \times 10^{15}$
N_2	$0{\cdot}40 \times 10^{16}$	
H_2O	?	

Total Mass of Atmosphere $= 6{\cdot}16 \times 10^{16}$ tonnes.

The present mass of the atmosphere is, as already stated, about $5{\cdot}2 \times 10^{15}$ tonnes, and this means that the original atmospheric pressure would be 61·6/5·2, or about 12 atmospheres. This figure has to be corrected for the CO_2 which would be in solution in the ocean. From the known solubility of CO_2 in fresh water, the ocean being at this stage presumably fresh, we can allow for this effect if we know the temperature of the ocean. Taking this temperature as

60° C., the ocean at this epoch being still presumably moderately hot, and the volume of the ocean as $1{\cdot}41 \times 10^{24}$ c.c., I find that the pressure would be reduced to about 10 atmospheres. For lower ocean temperatures the effect would be larger, thus for 30° C. the pressure would be about 9 atmospheres. Although this pressure may seem to be very large, it is very small compared with the pressure before the oceans had condensed, when it would have been of the order of 300 atmospheres. There is no question, either, of the CO_2 liquefying under a pressure of 10 atmospheres, since the boiling point of CO_2 at this pressure is about – 38° C., a temperature which we could hardly imagine being approached at any point on the earth's surface during this very early stage. The high atmospheric pressure thus deduced does not of itself present any grave objection to the theory, especially as it is a maximum figure.

B.—Distribution of Temperature and Water Vapour in the Primeval Atmosphere.

One of the governing factors of the amount of water vapour in the outer atmosphere is the temperature at the tropopause. The mathematical theory of an atmosphere in radiation equilibrium has been worked out by Gold (11). Regarding the atmosphere as consisting of two shells, the inner in the adiabatic state, and the outer in the isothermal, it is shown that for an atmosphere of uniform constitution, the adiabatic state could not extend to a height greater than that given by $p = \frac{1}{2}p_0$, where p_0 is the surface pressure. When the atmosphere is not uniform this height is increased. This lack of uniformity will be introduced by the variable concentration of water vapour with height, and Gold shows that, in this case, the adiabatic state cannot extend above a height given by $p = \frac{1}{4}p_0$. Whether Gold's arguments can be extended to the primitive atmosphere in which CO_2 is the predominant component is a question which needs further investigation, but we will probably not be very far wrong if we assume that the tropopause in this atmosphere occurred at a height where $p = \frac{1}{4}p_0$.

The height of the tropopause fixes the minimum temperature in the atmosphere, and thus the maximum density of water vapour at that height, since it cannot exceed the saturation value at this temperature. Gold (12) gives strong reasons for the saturation value being attained, and thus the saturation pressure at the tropopause gives us one important datum for the investigation of the concentration of water vapour in the upper layers. Above the tropopause the temperature starts to rise again, and hence in these layers the distribution of water vapour will be the same as that of a nearly perfect gas; since at no higher level will the saturation pressure be attained.

It can easily be shown that, given the ratio of the partial pressures of two gases at any level in an atmosphere in diffusional equilibrium, we can calculate this ratio at any level at which the partial pressure of one component is known, even if the temperature distribution is unknown. The height at which any

specified pressure will be attained will of course depend on the latter, and thus cannot be determined, but it will be seen in the sequel that the mere ratio is of some use.

Let us assume that the atmosphere is in diffusional equilibrium above the tropopause. Let p_0, θ_0, and ρ_0 be the pressure, temperature, and density of one gas at this height and p, θ, and ρ the corresponding quantities at any greater height. Further let p_0', etc., refer to the second gas. It is plain that $\theta_0 = \theta_0'$ and $\theta = \theta'$. Then we have, where p is the height,

$$dp = -\rho g\, dh = -\rho_0 \cdot \frac{p}{p_0} \cdot \frac{\theta_0}{\theta} \cdot g\, dh.$$

Thus,

$$\frac{p_0}{\rho_0} \cdot \frac{dp}{p} = -\frac{\theta_0}{\theta} \cdot g\, dh = \frac{p_0'}{\rho_0'} \cdot \frac{dp'}{p'}.$$

Now if R is the universal gas constant for one grammol and M is the molecular weight of the gas, then,

$$\frac{p}{\rho} = \frac{R\theta}{M}.$$

Hence,

$$\frac{1}{M} \cdot \frac{dp}{p} = \frac{1}{M'} \cdot \frac{dp'}{p'},$$

which gives on integration

$$\frac{p'}{p_0'} = \left(\frac{p}{p_0}\right)^{\frac{M'}{M}}.$$

Let us now apply this result to the existing atmosphere. For simplicity let us treat the nitrogen and oxygen of the atmosphere as one gas of molecular weight 29, and consider the concentration of water vapour, molecular weight 18 in the F layer. We know p_0, which is approximately $\frac{1}{4}$ of an atmosphere. We also know θ_0, the temperature of the tropopause, as about 220° K. This fixes p_0', which is the vapour pressure of ice at this temperature or about 0·03 mm. of mercury. Unfortunately we do not know p, the gross pressure of oxygen and nitrogen in the F layer, as though it is known that the number of molecules per c.c. is approximately 10^{11} (13), we cannot calculate the pressure in the F layer from the molecular concentration, unless we also know the temperature of the layer. Taking this to be 1000° K., and the number of molecules per c.c. of gas at N.T.P. as $2{\cdot}70 \times 10^{19}$, we find that $p = 1{\cdot}36 \times 10^{-8}$ atmosphere. Since $p_0 = \frac{1}{4}$ atmosphere, $p/p_0 = 5{\cdot}4 \times 10^{-8}$. Substituting this value in the equation,

$$\frac{p'}{p_0'} = \left(\frac{p}{p_0}\right)^{\frac{M'}{M}}$$

gives $p'/p_0' = 3{\cdot}2 \times 10^{-5}$, and since $p_0' = 0{\cdot}03$ mm. of mercury, or 4×10^{-5} atmosphere, nearly, this means that $p' = 1{\cdot}3 \times 10^{-9}$ atmosphere. Thus since $p = 1{\cdot}36 \times 10^{-8}$ atmosphere, this would mean that one molecule in ten in the F layer is an H_2O molecule. This is a rather surprising result, and probably not true. If such a quantity of H_2O were present, we would expect that hydrogen, supplied by its photo-dissociation, would also be present, and that the night sky spectrum would contain some hydrogen lines. This spectrum has been shown, however, by McLennan (14) to be mainly attributable to neutral molecular nitrogen and atomic oxygen. The discrepancy probably arises from the assumption that the mean molecular weight of the atmosphere is 29. In the upper layers the oxygen is mainly in the atomic form, although the nitrogen appears to be mostly in the molecular (6). This would have the effect of increasing the concentration of oxygen relative to both nitrogen and water vapour in the F layer. This effect does not lend itself to computation, as we are ignorant of the amount of oxygen dissociated at various heights. If we take the limiting condition that only atomic oxygen occurs above the tropopause, the previous method of calculation shows that in the F layer there will be one water molecule for every 25,000 oxygen atoms. It seems certain in any case that there is an appreciable quantity of water vapour present, and that even to-day the atmosphere must be losing small quantities of hydrogen, with a corresponding gain of free oxygen.

Turning now to the consideration of the assumed primitive atmosphere, the first point to be considered is the temperature of the tropopause in such an atmosphere. In a homogeneous atmosphere of molecular weight M in convective equilibrium, the temperature gradient is $g(\gamma - 1) \cdot M/R\gamma$, where R is the universal gas constant, and γ is the ratio of the specific heats. For the primitive atmosphere we may take $\gamma = 1{\cdot}3$ and M (the mean molecular weight) $= 35{\cdot}5$, which gives a temperature gradient of about $9{\cdot}7°$ C. per kilometre. The pressure p at any height h in the convective layer of any atmosphere is given by the relation,

$$h = \frac{\gamma}{\gamma - 1} \cdot \frac{R\theta_0}{Mg}\left[1 - \left(\frac{p}{p_0}\right)^{\frac{\gamma-1}{\gamma}}\right],$$

where p_0 and θ_0 are the pressure and temperature at the bottom of the atmosphere. If we assume that the tropopause occurs where $p = \frac{1}{4}p_0$, this equation gives the height of the tropopause in the existing atmosphere as about $9\frac{1}{2}$ kilometres, which agrees reasonably well with the observed value.

To calculate the height of the tropopause in the primitive atmosphere, we must however assume a value for θ_0. Presumably in the early stages of the earth's history after the condensation of the ocean, the surface temperature would have been a good deal higher than at present; so I will take $\theta_0 = 55°$ C. or $328°$ K. In Table 3 I give the results of applying these considerations to both the existing atmosphere and the primitive atmosphere.

TABLE 3.

	Present Atmosphere.	Primitive Atmosphere.
Average Molecular Weight	28·8	35·5
Ratio of Specific Heats	1·4	1·3
Surface Temperature. θ_0	280° K.	328° K.
Temperature Gradient. (*a*) Calculated	$9{\cdot}75 \times 10^{-5}$	$9{\cdot}70 \times 10^{-5}$
(*b*) Observed	$5{\cdot}0 \times 10^{-5}$	—
Height of Tropopause. Calculated	9·4 km.	9·9 km.
Temperature of Tropopause. (*a*) Calculated ...	188° K.	241° K.
(*b*) Observed ...	220° K.	273° K. (?)
Vapour Pressure of H_2O at Tropopause	0·03 mm.	4·6 mm. (?)

It will be noticed that the calculated temperature gradient in the existing atmosphere is about 10° C. per kilometre. In practice, however, due to the presence of water vapour and other causes, this limiting gradient is not reached, the actual gradient being about 5° C. per kilometre. Since the calculated values for the temperature gradient and the tropopause height for the primitive atmosphere are so similar to those of the present atmosphere, I have assumed, perhaps rather rashly, that the actual temperature gradient in it would also be about 5° C. per kilometre. This would lead to a tropopause temperature of about 0° C. or 273° K., taking the surface temperature as 55° C. The corresponding water vapour pressure would be 4·6 mm. or 6×10^{-3} atmosphere.

We are now in a position to discuss the possible constitution of the F layer in the primitive atmosphere. It seems clear that, given a fixed amount of solar radiation, the position of this layer will be fixed at the level where the molecular concentration attains a figure of about 10^{11} per c.c., as in the present atmosphere. We will also take the temperature of the layer to be 1000° K., as before. From the relation

$$\frac{p_1'}{p_0'} = \left(\frac{p_1}{p_0}\right)^{\frac{M'}{M}},$$

we can, if we know the tropopause pressure and the F layer pressure for any one component of the atmosphere, calculate the corresponding ratio for any other component. In Table 4 I have taken the concentration of methane in the F layer to be 10^{11} molecules per c.c., and calculated the values for the other components. It is to be noticed that the validity of this method depends on the assumption that every component gas is in its own diffusional equilibrium independent of the presence of the other gases.

TABLE 4.

	CO_2	CH_4	N_2	H_2O
Molecular Weight ...	44	16	28	18
Total Mass in 10^{16} tonnes	4·2*	0·72	0·4	—
Surface Pressure†	8·1	1·4	0·8	—
Tropopause Pressure. Temp. 273° K. ...	2·0	0·35	0·2	6×10^{-3}
F layer Pressure. Temp. 1000° K. ...	$8·4 \times 10^{-21}$	$1·36 \times 10^{-8}$	$2·2 \times 10^{-14}$	$2·8 \times 10^{-11}$
Molecules per c.c. in F layer ...	$6·2 \times 10^{-2}$	10^{11}	$1·4 \times 10^{5}$	$2·1 \times 10^{8}$

* This figure has been corrected for the CO_2 dissolved in primitive ocean at temperature of 60° C.

† All pressures given in atmospheres.

It will be seen that the F layer consists nearly entirely of CH_4, with about one H_2O molecule in 500, one nitrogen molecule in a million, and a vanishingly small amount of CO_2. This latter fact shows that the photo-chemical reactions of CO_2 in the upper ionosphere are of little importance.

Since the presence of the assumed large amount of CH_4 in the primitive atmosphere is doubtful, I have also calculated the composition of the layer, assuming that no CH_4 was present in the primitive atmosphere, the amounts of the other components being unchanged. In this case the concentration of H_2O, being now the lightest component, has been taken as 10^{11} in the F layer. The figures in this case are—

	CO_2	N_2	H_2O
Molecules per c.c. in F layer	$2·2 \times 10^{5}$	$2·6 \times 10^{9}$	10^{11}

Again we see that the amount of CO_2 is very small, but in this case the main component of the layer will be H_2O. This is a condition much more favourable to the production of free oxygen by photo-chemical dissociation than when a large amount of CH_4 is present. The bearing of these figures on the possible rate of liberation of free oxygen in the atmosphere will be discussed later. It may be noticed that the concentration of nitrogen in both cases is probably underestimated, since it has been taken that all the nitrogen is present in the molecular form, whereas it is likely that at all levels some of it will be in the atomic form. This fact would lead to a higher value for the nitrogen concentration in the layer. Judging from the fact that few of the nitrogen molecules in the present atmosphere appear to have dissociated into the atomic form, even in the F layer, it seems that the correction to be applied to the calculated nitrogen concentration in the primitive atmosphere will not be important.

In all the previous argument it has been assumed that the outer layers of an atmosphere exposed to solar radiation will be at a high temperature as compared to ordinary terrestrial surface temperatures. The experimental evidence at present available is fairly conclusive in proving that this view is correct for the present atmosphere. It might be urged, however, that it need not necessarily be true for the primitive atmosphere.

The mechanism by which the present F layer of the atmosphere is raised to this temperature is, as yet, not entirely understood. The explanation usually given is that it is due to the selective absorption of gases such as oxygen and ozone in the region below 3000 A. (15). Oxygen and nitrogen possess no infra-red spectra, and consequently no spectra through which they could radiate energy at temperatures as low as 1000° K. This is confirmed by the fact that it is impossible to cause a gas, such as oxygen, to emit its optical spectrum by any temperature which can be attained in the laboratory. If we then assume that the ultra-violet energy absorbed can be converted into thermal agitation of the molecules, we have a mechanism by which an atmosphere of pure oxygen and nitrogen could reach a very high temperature. The polyatomic gases, such as O_3, CO_2, CH_4, and H_2O, can radiate in the infra-red, and consequently their presence will limit the temperature attained. The effect of these gases is complicated by the fact that they will also increase the absorption of solar energy. It seems plain, however, that the presence of large quantities of H_2O in the F layer would lower the temperature, since the absorption and radiation from the layer would then approximate more closely to that of a black body, and the black body temperature of solar radiation near the earth is about 280° K. This view shows that there would probably be an optimum water vapour concentration in the F layer which would give the maximum rate of free oxygen production, since increasing the figure above this value would lower the temperature, and the effect of the increase of the percentage of dissociated water vapour would be overweighted by that of the decrease of the rate of escape of hydrogen. Thus a slower net gain of free oxygen would result. It is possible, therefore, that the greatest production of free oxygen by dissociation did not occur till the earth's surface had cooled considerably, and thus decreased the amount of H_2O in the F layer.

There is another effect which, however, would tend to increase the rate of escape of hydrogen. If free hydrogen were present in any appreciable quantity in the F layer, above a certain level in the outer atmosphere, the atmosphere would become nearly pure hydrogen, due to its low molecular weight. It seems probable that the temperature would be considerably higher here than in the F layer, since the hydrogen atmosphere could still gain thermal energy by absorption of short ultra-violet, which it could not get rid of by radiation, there being no polyatomic molecules present. The chief method by which it could lose heat would be by conduction to the layers at lower temperature below. It seems impossible at present to calculate whether this would be sufficient to prevent any considerable rise of temperature occurring, since we are ignorant of the rate at which thermal energy is produced here. The effect of conduction is not entirely negligible, however. Thus it can be shown that, due to conduction only, the average temperature of the atmosphere above the existing F layer would fall by about 3° K. per hr. during the night. This rate of loss of energy has little controlling effect on the F layer temperature, since it is known that the nightly variations are much greater than this figure

would indicate, and consequently the energy input during the day must greatly exceed the heat conduction loss, the main temperature controlling agent being the radiation of the polyatomic molecules. The same conclusion cannot be hastily applied to the postulated hydrogen atmosphere, in which the energy intake would presumably be far less, since most of the hydrogen would be in the atomic form, and only able to absorb in the extreme ultra-violet. In any case the density of this very high level would be excessively low, and if the escape of hydrogen only occurred from this level, the mass escaping would be correspondingly small. We will assume, consequently, that the rate of escape of hydrogen mainly depends on the quantity of it present in the F layer, and on the temperature of this layer. It will also be taken that the temperature of the outer atmosphere is, at least, not lower than the temperature of the F layer.

C.—Rate of Escape of H from the F Layer at a temperature of 1000° K., and consequent Rate of Liberation of Free Oxygen in the Atmosphere.

Jeans has shown (4, p. 342, *et seq.*) that the time required for a planet to lose any given component of an isothermal outer atmospheric layer is given approximately by the expression,

$$t_1 = \frac{1\,45\,C}{g\left(1+\frac{3ga}{C^2}\right)} \cdot \exp \frac{3ga}{C^2},$$

where t_1 = time of escape, C = molecular velocity of component gas, g = gravitational acceleration, and a = radius of planet. This gives $t_1 = 4{\cdot}75$ years, say 5 years.

Let n_0 = number of H molecules per c.c. at base of assumed isothermal layer, i.e., at F layer level.

M = total mass of hydrogen above 1 cm.^{2} of F layer.

p_0 = partial pressure of hydrogen in F layer.

k = Boltzmann's Constant = $1{\cdot}37 \times 10^{-16}$.

θ_0 = temperature of outer isothermal atmosphere.

We have, $Mg = p_0 = kn_0\theta_0 = 1{\cdot}37 \times 10^{-13} n_0$.

This gives $M = 1{\cdot}4 \times 10^{-16} n_0$ grams. The escape of this hydrogen will liberate eight times its mass, i.e., $1{\cdot}1 \times 10^{-15} n_0$ gram of oxygen per square centimetre of the earth's surface every five years. The total mass of oxygen per square centimetre of surface at present is about 200 g. This gives us the time required to produce all the oxygen at present in the atmosphere as $5 \times 200/(1{\cdot}1 \times 10^{-15} \times n_0) = 9 \times 10^{17}/n_0$ years.

The molecular concentration in the F layer has been taken as about 10^{11}. Thus we see that if one molecule in a hundred was a dissociated water molecule, n_0 would be equal to 10^9, and the time taken to produce our present atmosphere

about 900 million years, approximately half the estimated age of the earth. It is not, however, suggested that the bulk of the free oxygen in the present atmosphere has been evolved by this mechanism. This method would be only required to produce enough oxygen to allow of the start of plant life, the major part of the oxygen being subsequently liberated by chlorophyl photo-synthesis. It is impossible to state what percentage of the present atmospheric oxygen content would be sufficient for early plant forms, but if we took it as, say, 10%, one dissociated water molecule per 1000 in the F layer would account for its formation in 900 million years. It seems possible, therefore, that the process is capable of furnishing the amount of oxygen required.

There are two other factors, however, which must be considered. Firstly, Jeans, in deducing the time of escape of an atmosphere, assumes that the gas considered is in diffusional equilibrium. When the time of escape is of the order of thousands or even millions of years, this assumption introduces no serious error, but for times as short as five years the effect of the rate of diffusion of hydrogen from the lower level F layer, where it would be mainly produced, to the limits of the atmosphere where it would escape, might easily decrease very largely the amount escaping. One would imagine also that this effect would be greater the lower the percentage of hydrogen in the F layer, since the coefficient of diffusion of hydrogen into, say, nitrogen is less than that of hydrogen into hydrogen.

The second factor is that possibly a large proportion of any hydrogen present in the F layer would be in the atomic and not the molecular form. The dissociation energy of O_2 is 5·09 electron volts, that of H_2 4·46 electron volts (16). Now it is usually held that most of the oxygen in the existing F layer is in the atomic state (6, p. 59). Since the dissociation energy of a hydrogen molecule is less than that of an oxygen one, it seems possible that any hydrogen in the layer would also be largely in the atomic form. The thermal velocity of a hydrogen atom at any temperature is $\sqrt{2}$ times that of a hydrogen molecule. Owing to the importance of the exponential term in Jeans' formula, this would reduce the time of escape of the hydrogen from five years to about two days, i.e., by a factor of about $\frac{1}{100}$.

We might then, at least, conclude that the effect of the second factor would balance the effect of the first, so that our previous conclusion that the proposed mechanism should be capable of providing enough oxygen to start plant life in about 900 million years would still stand.

The assumption that the postulated concentration of hydrogen in the F layer could be maintained for long geological ages is, however, open to question. The problem is a difficult one, depending as it does not only on the rate of dissociation of H_2O molecules but also on their rate of recombination. Some figures on the purely thermal recombination of an electrolytic mixture of hydrogen and oxygen at normal pressure are due to H. Helier (17). He found that equilibrium was attained at 910° K. when 85·6% of water had been formed, the corresponding figure for 1100° K. being 96·1%. The formation of the

water, however, mainly occurs on the heated surface of the solid container. It seems probable, therefore, that the equilibrium attained in the absence of such a container would contain a much smaller percentage of water. Unfortunately in the F layer the case is complicated by the presence of ultra-violet light, which would tend to produce recombination as well as dissociation. Thermal dissociation of the water vapour is apparently of little importance. Nernst and von Wartemberg (18) have shown that the degree of dissociation, x per cent., is given, when x is small, by the relation, $k = px^3$, where p is the pressure in atmospheres, and k is a constant depending on the temperature. For 1000° K., $k = 2{\cdot}7 \times 10^{-14}$. If we take the extreme case when the concentration of H_2O molecules is 10^{11}, the layer being nearly pure water vapour, then $p = 1{\cdot}36 \times 10^{-8}$ atmosphere, which gives $x = 1{\cdot}26 \times 10^{-2}$. Thus the number of dissociated molecules per c.c. would be $1{\cdot}26 \times 10^7$, or about $\frac{1}{10}$ of the previously postulated value. Decreasing the value of p will lower this figure, since it is easily seen that the concentration of dissociated molecules is proportional to $p^{\frac{1}{3}}$. Furthermore, as previously indicated, such a large concentration of H_2O in the F layer would probably lower the temperature so much that the escape of hydrogen would become excessively slow, and thus it is only much lower values than 10^{11} which might lead to the formation of free oxygen at any appreciable rate.

The value of the optimum concentration of water vapour must remain uncertain. It is, I think, clear that, if the water vapour in the F layer and above it is capable of absorbing nearly all the radiation which produces dissociation, increasing the vapour content will, as already mentioned, lower the rate of production of oxygen due to the lowering of the F layer temperature. In the same way a large proportion of CH_4 in the layer would lower the temperature, since CH_4 possesses a rotation-vibration spectrum in the near infra-red, by which it could get rid of thermal energy. This is an argument in favour of considering that the primitive atmosphere contained no methane, but, as already indicated, this leaves the carbon/oxygen ratio unexplained. It seems uncertain, however, that an outer atmosphere consisting of nearly pure CH_4 could attain a sufficient temperature to enable the hydrogen produced by its photo-dissociation to escape in any reasonable time. If this conclusion is correct, the primitive atmosphere must have contained no CH_4. It must also be remembered that we know very little even to-day of the amount of energy in the solar spectrum capable of producing dissociation, and, we may say, nothing about the corresponding quantity in the early stages of the earth's history, when presumably the sun's condition was very different from its present state.

It will be seen that there is no difficulty in a methane-free primitive atmosphere of enough water vapour being present in the upper layers to give the required concentration of dissociated hydrogen, provided the radiation could produce it. It has been shown that, in this case, the primitive F layer would be nearly pure water vapour with very little nitrogen. As the

earth's surface temperature fell the amount of water vapour in the layer would decrease, till finally the optimum value for oxygen production would be reached; and a state approximating to this might continue for long periods. Thus we see that the rate of production of free oxygen would at first be small, due to the low F layer temperature, rising to a maximum as the water vapour concentration fell and the temperature rose, and finally falling again as the layer became impoverished of water. Even at present some free oxygen must be produced in the F layer, since there is good evidence for the view that about one molecule in 6000 is water vapour (19). Thus we see that the rate of growth of oxygen would be a slow process, and that the maximum rate would not occur in the very early stages.

It must be pointed out that, as already stated, the constitution of the F layer of the primitive atmosphere has been calculated on the assumption of diffusional equilibrium above the tropopause. Godfrey and Price (15, p. 232), however, consider that the concentration of water vapour in the F layer should be calculated on the assumption of perfect mixing even up to the F layer. If we apply this method to the primitive atmosphere it would lead to the layer being mostly composed of CO_2. This gas is a very good thermal radiator possessing a vibration-rotation spectrum in the near infra-red, and possibly also a pure rotation spectrum in the far infra-red. The presence of CO_2 in the F layer would, accordingly, probably tend to lower the temperature of the layer greatly. It seems unlikely, however, owing to its high molecular weight, that perfect mixing of the CO_2 would occur to such high levels. Chapman holds that the experimental results on the oxygen content of the present atmosphere show that partial diffusive separation begins to occur at heights above about 20 km. (6, p. 49). Unless therefore the process is arrested in some higher layer, where the conditions favour an upward increase of turbulence and mixing, the assumption of diffusional equilibrium, I have made, seems to be a fair working hypothesis.

D.—Photo-dissociation of Water Vapour.

The types of radiation which can produce dissociation of water vapour may now be briefly considered. Rathenau has shown that water vapour possesses an absorption band between 1770 and 1540 A, which dissociates it, probably into H and OH (20). The OH molecule might itself be subsequently further dissociated, since the energy for this process is slightly less than that required for H_2O. Rathenau gives the relevant values as $D_{H_2O} = 5$ volts and $D_{OH} = 4{\cdot}9$ volts. Alternatively, if two OH molecules combined, H_2O_2 would be formed, which would probably quickly dissociate into H_2O and O. This absorption band would seem to be the most likely to produce the major part of the dissociation, since it is likely to be present in far greater quantities than those of shorter wave-length. Thus water vapour has absorption bands in the region $\lambda < 1400$, which eventually fuse into an ionisation continuum just below 1000 A. Absorption regions from 860 to 740 A and 694 to 504 A also

occur. All these bands probably cause dissociation, but Chapman (6, p. 63) concludes that they probably have little importance for the earth's present atmosphere, owing to the small amounts of these wave-lengths in the solar spectrum. It does not follow, of course, that they would have been absent from it in earlier geological ages; in fact our knowledge of solar radiation in space is still very limited, due to the complete absorption of its shorter components by the atmosphere. Thus it is possible that in the primitive atmosphere the shorter wave-length bands were important.

Some evidence of the character of the solar radiation can be obtained from our knowledge of the state of ionisation of the F layer. It has been established that the negative ions present in the layer are mostly free electrons, there being about one electron per 10^5 molecules at periods of maximum ionisation. The most direct method of producing these free electrons would be by photo-electric emission from the gas molecules. To effect this would, however, entail the presence of wave-lengths less than 1000 A, since the photo-electric thresholds of atmospheric gases are below this figure. Thus for O_2 the threshold value is 990 A, and for N_2, 760 A. It has, however, been shown by Hughes (21) and others that air can be ionised by light of longer wave-length than 1250 A, but shorter than 1450 A. He sets the probable threshold value at about 1350 A. The emission of electrons by these wave-lengths can be explained by the hypothesis that it is due to one molecule absorbing two quanta, the first of which raises it to an excited state and the second causing the ejection of the electron. It is also possible that the collision of two excited molecules might lead to the ejection of a free electron. The question, whether either of these two effects would be sufficient to account quantitatively for the observed electron concentration, requires further investigation, but at least we are justified in concluding that wave-lengths of the order of 1300 A are present in fairly large amounts in the F layer, and consequently that the band 1770–1504 A, which produces dissociation of water vapour, is present in larger amounts.

Corpuscular radiation from the sun is also capable of producing dissociation. At present it is held that most of the ionisation, and presumably also most of the dissociation in the F layer, is due to ultra-violet light. Again, however, this conclusion might not be applicable to the sun in earlier ages. The most recent work on the ionisation and dissociation by electron impact of water vapour is due to Mann, Hustrulid, and Tate (22). They have observed nearly all the theoretically possible reactions ranging from $H_2O \rightarrow OH + H^-$ at 5·7 volts to $H_2O \rightarrow H^+ + H^+ + O^-$ at 36·0 volts. Two processes which would apparently easily lead to the liberation of free oxygen in the F layer are $H_2O \rightarrow H_2 + O^+$, at 18·8 volts, and $H_2O \rightarrow 2H + O^+$, at about 28 volts, since in both these reactions the O^+ could be subsequently neutralized by combination with a negative electron. There is, moreover, little doubt that solar corpuscular radiation would possess sufficient energy to produce such reactions, since even a 100-volt electron is a comparatively slow one.

We may fairly conclude from the above data that dissociation of water vapour must occur in the F layer, but again our present knowledge leaves the quantitative position very uncertain.

E.—Astronomical and Geological Evidence.

It has been shown recently that the presence of large quantities of free oxygen in a planetary atmosphere is practically restricted to the earth. The atmospheres of the major planets consist apparently mainly of CH_4 with a certain amount of NH_3. This fact is attributed to the power of these planets of retaining hydrogen owing to their larger masses. It may also be noted that the effect of solar radiation on the temperature of the outer layers of their atmospheres will be small, owing to their distances from the sun. There is apparently some oxygen in the atmosphere of Mars, and possibly also some water vapour. The amount of both is, however, small compared with the earth's atmosphere. The moon and Mercury possess no atmosphere, being too small to retain one. Mercury, due to its proximity to the sun, also suffers from the disability of a high surface temperature. Venus possesses, apparently, a fairly dense very cloudy atmosphere, the actual surface of the planet being never visible. The peculiar fact is that neither water vapour nor oxygen can be detected in its atmosphere above the cloud level. The main component is apparently CO_2, and the nature of the clouds is unknown, although it seems unlikely they could be water. Venus is thought to take about 23 days to rotate, and consequently it might be expected that the temperature changes in its atmosphere would be much larger than those in the earth's atmosphere. The planet is also a good deal closer to the sun than the earth, and this suggests that possibly during the long solar day some portions of its outer atmosphere become so hot that not only hydrogen but also atomic oxygen and water vapour can escape at appreciable rates. This would explain the absence of these gases from its outer atmosphere, which is the only portion of it open to investigation.

Turning to the geological side of the question, we would imagine that if free oxygen only developed slowly in the atmosphere we should find some evidence of this fact in the geological history of the earth. It may be taken, I think, that the existence of life implies the presence of appreciable amounts of free oxygen. As far as can be seen at present this view rather favours the slow development of free oxygen, since before Cambrian times fossil remains are very scarce. The age of the ocean is usually considered to be about 2000 million years, whereas the Cambrian is only between 500 and 600 million years old.

Naturally we cannot assume that the absence of fossil remains in the rocks of certain epochs proves the absence of life in any form on the earth at that epoch, since soft-bodied forms of life may have existed. These would presumably leave no trace in the geological records. It is accordingly justifiable to conclude that life appeared a long time before Cambrian times, but even if we placed its birth at about 1000 million years, this would still leave a period of 1000 million years for the development of enough free oxygen to enable low

forms of life to exist. Land plant forms do not appear until Silurian times, but it is usually held that green algae, capable of breaking down CO_2, existed long before this period. As far as I am aware, however, no direct evidence of the existence of any form of life during the first half of the existence of the ocean is available, so that the theory of the gradual evolution of the atmosphere, I have advanced, is, at least, not contrary to the geological evidence.

Summary.

It is known on geochemical grounds that it is highly probable that the primitive atmosphere contained no free oxygen. An attempt is made to calculate its constitution from the available data supplied by the average composition of the igneous and sedimentary rocks of the lithosphere and the probable total amount of igneous rocks denuded during geological time. From these considerations it is shown that the total amount of free carbon at present buried in the sedimentary rocks could not have been derived from the CO_2 present in the primitive atmosphere. It is suggested that, possibly, a large quantity of methane was present in this atmosphere, but grave objections to this view are also advanced. The growth of free oxygen in the atmosphere is discussed. The original liberation of free oxygen is attributed to the photo-dissociation of water vapour in the upper atmosphere, combined with the probably high temperature of this region, which leads to the gradual escape of hydrogen, thus leaving free oxygen behind in the atmosphere. It is assumed that by this method enough oxygen could be finally accumulated in the atmosphere to enable plant life to start and then produce by the photo-synthetic decomposition of CO_2 the main part of the free oxygen, which is at present in the atmosphere, or has been used up during geological time in the formation of the sedimentary rocks. The various problems, involved in this theory, are considered, as far as possible, from the quantitative point of view. It is thus shown that the original accumulation of free oxygen would have been a slow process. This view agrees with the fact that there is no evidence to show that life existed on the earth during, at least, the first half of the age of the ocean. The apparent absence of both oxygen and water vapour from the outer atmosphere of Venus is also, very briefly, discussed. In the present state of our knowledge, however, the views advanced in this paper can only be considered as highly speculative.

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No. 37.

STUDIES IN PEAT.

Part 10.

ACTIVATED CHARCOALS FROM PEAT RESIDUE.

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Processes for activating charcoals fall into two distinct classes, in each of which certain special methods have become standardised. In chemical methods of activation the raw material is impregnated with various substances—zinc chloride and syrupy phosphoric acid are widely used—before carbonization. When zinc chloride is employed the carbonization temperature lies between 400° and 800° C., and the zinc oxide remaining is leached out with acid; H_3PO_4-treated[1] materials on the other hand are given an 8–10 hour carbonization at a final temperature of approximately 1,000° C. The acid is reduced, phosphorus distils off, and may be re-oxidised to the acid.

In the second, more flexible and perhaps more widely used method, activation is effected by the oxidising action of air, steam, or flue gases at high temperatures on the primary carbon, which must have been liberated at a temperature not exceeding 600°–700°. In general, the activity of the product increases with time of steaming and at the expense of the yield and the bulk density.

Quite different from either of these is Radbruch's method (Z. angew. Chem., 1939, p. 590) of obtaining a decolorizing carbon from peat by treatment with warm concentrated sulphuric acid.

The peat residue used as starting material in the present investigation is, as far as we know, the first substance of Irish origin to be examined as a source of active charcoal, and in working with it we aimed more at finding in broad outline the best methods of activating this type of material rather than at working out the details of one or two processes, details which in any event would probably have to be modified in using other apparatus.

The general plan of the investigation was as follows:—

Effect of treatment with concentrated sulphuric acid at different temperatures.

Effect of varying the proportion of impregnating agent and the temperature of carbonization on charcoals activated with zinc chloride and phosphoric acid.

Effect of time and temperature of steaming, and size of charcoal granule, in steam activation.

[1] This notation is employed throughout in the interests of brevity.

The estimation of the true activity of a charcoal is very difficult; the order of activity of two carbons may be reversed in different solutions, and two carbons which have the same adsorptive efficiency at a given concentration of sorbate may differ widely in performance at other concentrations. The charcoals prepared in the present work were submitted to three tests, in every case in comparison with commercial standards:—

I. Bulk density of 180–270 mesh fraction. This is of value as affording a measure of the porosity of the charcoal.
II. Determination of the phenol isotherm.
III. Determination of the decolorizing power towards dilute solutions of molasses.

Experimental.

Nature of Raw Material.

A note is necessary on the origin of the residue. In the extraction of wax from peat the most suitable raw material has been found in peat from the Lyrecrumpane Bog, Co. Kerry. After extraction of the wax present with ethyl alcohol and steaming to remove the residual solvent, the residue remains as a dark brown, fairly finely ground material, containing about 5% of apparently undecomposed fibrous matter. Much of it is fine dust, and the largest lumps measure only about half a centimetre. The packing density is 0·5 g./c.c.

Two lots, taken at different times, agreed in all the above particulars, but differed in the ash content:—

First Lot: ash on anhydrous residue = 6·50%. Ash light red.
Second Lot: „ „ „ = 3·35%. Ash dark red.

The first lot was used exclusively for the zinc chloride and steam activations; the second only for treatment with sulphuric and phosphoric acids.

All the residue was dried for 2–3 hours at 110°–120° before use.

Activation with Warm Concentrated Sulphuric Acid.

This process, since it differs radically from other methods of activation, is considered separately. Three lots of residue (second batch) were activated by this method. The raw material in all cases was ground till more than 80% of it passed a 30-mesh screen, and dried again before adding to the concentrated acid, which was contained in a beaker in an oil bath. Frequent stirring with a thermometer is necessary to prevent local overheating of the pasty mass produced. The addition of the residue to the acid causes a sharp rise in temperature, accompanied by evolution of sulphur dioxide, which

continues to come off during the whole of the heating period. When heating was finished the beaker was emptied into a large quantity of cold water, and the product washed by decantation and with hot water at the pump till free of sulphate. It was then dried, ground till all passed a 180-mesh screen, and dried again for 2 to 3 hours at 110°–120°.

A. 50 g. residue was added to 150 c.c. concentrated acid and kept at 50–60° for 1 hour with frequent stirring.

B. 50 g. in 150 c.c. acid was kept at 80–90° for 1 hour, as above.

C. 50 g. in 150 c.c acid was kept at 110–120° for 1 hour.

Very prolonged washing is necessary to remove the last traces of sulphate. A and B, but not C, gave a persistent yellow-brown colour to the wash-water. All had a peculiar sweet smell when wet, but the dust produced during grinding had a sharp odour.

Note on Nomenclature.

In all cases the name of the primary substance is given first, then follows the maximum temperature of treatment, and finally the number of minutes for which this temperature was held. E.g., a-$ZnCl_2$/450°/60 denotes the charcoal obtained when the a-$ZnCl_2$-treated residue was held at 450° for 60 minutes. Similarly PC/SA 800°/30 means primary charcoal, steam activated at 800° for 30 minutes.

Preparation of the Starting Materials.

a-$ZnCl_2$. 300 g. dried residue was added to a solution of 120 g. anhydrous zinc chloride in 400 c.c. water plus a few drops of hydrochloric acid. After thorough mixing the damp mass was dried on a tray for two days at 30°, and finally at 100°, to give a very friable product. The yield was 94% of the weight of residue and zinc chloride used.

b-$ZnCl_2$. Here only 60 g. zinc chloride was used for 300 g. residue, otherwise the treatment was the same as the above. The yield, calculated as above, was 93%.

In both cases there was no appreciable heat evolution on mixing, and no change of note in the appearance of the residue.

a-H_3PO_4. 300 g. residue, ground till more than 80% of it passed 30 mesh, and dried, was added to 300 c.c. of concentrated phosphoric acid (sp. gr. = 1·75) and mixed thoroughly in a shallow dish to form a dark pasty mass. After drying for two days at 100–120° the product was brownish-black, dry, and much of it in fairly hard lumps. The yield was 84% of the weight of residue and phosphoric acid taken.

b-H_3PO_4. Here the quantity of phosphoric acid used was only half that employed in the a-H_3PO_4 treatment; in other respects conditions were practically

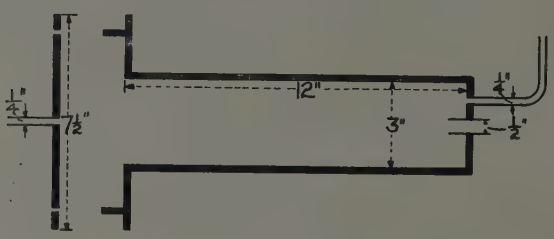
identical. After drying, however, there was no loss in weight and no formation of lumps.

Preparation of Primary Charcoal (P.C.).

The preliminary carbonization of that part of the first batch of residue intended for steam activation later was carried out in the furnace of Reilly and Donnelly (Sci. Proc. Roy. Dub. Soc., **19**, 29, 1930). For various reasons the temperature was not regulated very accurately, though the point is probably of minor importance. All lots, however, were treated somewhat as follows:— Two to three hours heating in a current of coal gas to 400°, then kept at 400–420° for 2–3 hours longer, still with gas passing. Carbonization appeared to be complete after this length of time, the average yield being 46 ± 2% on the weight of dried residue in the charge. The separate lots were mixed thoroughly before storing in tightly-closed tins.

Description of the Furnace.

This was specially designed, and used for the heat treatment of all but the primary charcoal; it resembles somewhat the retort used by Ardagh (J.S.C.I., 1921, p. 230 T). A 12″ length of 3″ steam pipe was closed at one



end by a welded-on stop, at the other by a flange to which a circular cover-plate could be bolted, the joint being made gas-tight with an asbestos washer. Short lengths of ¼″ pipe served as inlet and outlet, and in addition the small end was fitted with a short sleeve to carry the thermocouple.

A length of 4″ asbestos piping enclosing the retort carried the electrical winding. This was in two sections, each covering half the furnace chamber and consisting of about 70 ft. of No. 19 S.W.G. 80/20 Nichrome wire, crowded together somewhat at the outer ends to compensate for increased radiation losses there. After winding, the retort was enclosed in a sheet steel drum 9″ in diameter, packed with asbestos. The ends were likewise heavily lagged. The leads were brought to three terminals on the outside of the furnace, and so arranged that the windings could be put either in series or parallel as desired.

Two external series resistances, one coarse and one fine, served to control the furnace temperature. The thermocouple used to measure this was a

platinum—platinum-iridium type used in conjunction with a millivoltmeter reading to within 5° C. The hot junction was at the centre of the chamber, but, in any case tested, no temperature gradient along the furnace could be detected.

The asbestos pipe as a core for the windings was adopted after the mica first tried had broken down. Its strength, convenience, and ability to withstand high temperatures without breakdown go far to outweigh its poor thermal conductivity.

Preparation of Charcoals.

Irrespective of origin, all carbons prepared were treated as follows:—

> Crude charcoal from carbonization acid-extracted by standing in warm, moderately dilute hydrochloric acid for one or two days. Then filtered, and washed with hot water at the pump till no excess chloride could be detected in the runnings. Dried and ground in a mortar till all passed 180 mesh. Finally dried at 100–120° for two to three hours and bottled.

The duration of heating varied with the material being carbonized; for example, $ZnCl_2$-treated batches got 1–1½ hours pre-heating before being held at the desired temperature for one hour, while H_3PO_4-treated residue was carbonized for eight to nine hours with the temperature rising steadily to the maximum, at which it was held for 30 minutes. In all cases where tar was being evolved a slow current of coal gas was maintained through the furnace till heating had ceased.

Steam Activation.

The activating effect of steam is due most probably to its oxidising action on tarry hydrocarbons fouling the carbon surface. The main reaction $C + H_2O \rightleftarrows CO + H_2$ in this oxidation is affected by time, temperature, rate of steam flow, accessibility of steam to carbon, and other factors. Good circulation of steam is of obvious importance, but the industrial methods of securing it (rotating the retort, etc.) are not easy to reproduce on a small scale. The rate of steam flow is more important at temperatures above about 850°, when equilibrium is rapidly attained and an inadequate steam flow may slow up the activation considerably. We do not know of any published work on the effect of grain size on activation, but obviously the interior of a large granule cannot—even allowing for diffusion—be as well activated as the surface. This less activated carbon will form the coarser fraction in grinding, and consequently one may expect that the bulk density of such a char will be disproportionately high.

Experiment justified all these conclusions. In the earlier experiments (30-minute chars) the ungraded primary charcoal was loaded to a depth of

3 to 4 mm. on two flat steel trays inserted in the furnace. Though the steam flow was kept roughly constant, and gas circulation over both trays was unhindered, the position of the steam inlet obviously favoured the upper tray, and a much greater percentage of the carbon on it was gasified, especially at higher temperatures.

In an effort to secure better exposure of charcoal to steam, the primary carbon for the 60-minute activation was screened, and the on-10 mesh fraction used, loaded as before. The difference between the trays persisted, however, while the yield was, as might be expected from the lower ratio of surface to mass, greater.

In all cases the chars from the two trays were mixed before extracting with acid.

The superheater used in these experiments was an 18″ length of ½″ steam pipe, heated in an ordinary laboratory combustion furnace. With a little experience the superheater temperature can be regulated fairly well, though some muffling is necessary when working at 950°.

Results.

Only the most significant features in a considerable amount of experimental data can be given here.

Percentage Yields.

All the following are calculated as weight of finished charcoal on weight of dried residue taken. The figures for the steam-activated carbons should be considered in the light of the discussion earlier:—

Charcoal.	*Per Cent. Yield.*
H_2SO_4-activated carbons—A, B, C, ...	70–75%.
$ZnCl_2$-treated charcoals	53–33%.[2]
H_3PO_4-treated charcoals	50–55%.
Steam-activated charcoals	13–21%.

Appearance of Charcoals Prepared.

H_2SO_4-treated carbons are brownish-black and hard.

$ZnCl_2$-treated carbons were black, with a greyish lustre, and rather hard.

H_3PO_4-impregnated charcoals were remarkably grey and extremely hard. b-H_3PO_4/950°/30 is abnormal in this as in other respects; there was probably some undetected mishap in igniting it.

All the steam-activated charcoals are dull black and soft.

[2] The yield decreased with increasing temperature.

Bulk Densities.

These were determined by taking 7–10 c.c. of the 180–270 mesh fraction of each charcoal and tapping it down to constant volume in a 10 c.c. measuring cylinder of about 1 cm. diameter.

Charcoal.	*Bulk Density.*
A, B, C	0·762 ± 0·020
a-$ZnCl_2$/350°/60	0·621
a-$ZnCl_2$/450°/60	0·540
Other a-$ZnCl_2$ carbons	0·575 ± 0·006
b-$ZnCl_2$ carbons	0·637 ± 0·007
a-H_3PO_4/750°/30	0·583
a-H_3PO_4/850°/30	0·446
a-H_3PO_4/950°/30	0·538
b-H_3PO_4/850°/30	0·615
b-H_3PO_4/950°/30	0·400
PC	0·630
PC/SA 800°/30	0·505
PC/SA 850°/30	0·460
PC/SA 900°–920°/30	0·447
PC/SA 950°/15	0·483
PC/SA 800°/60	0·545
PC/SA 850°/60	0·530
PC/SA 900°/60	0·494

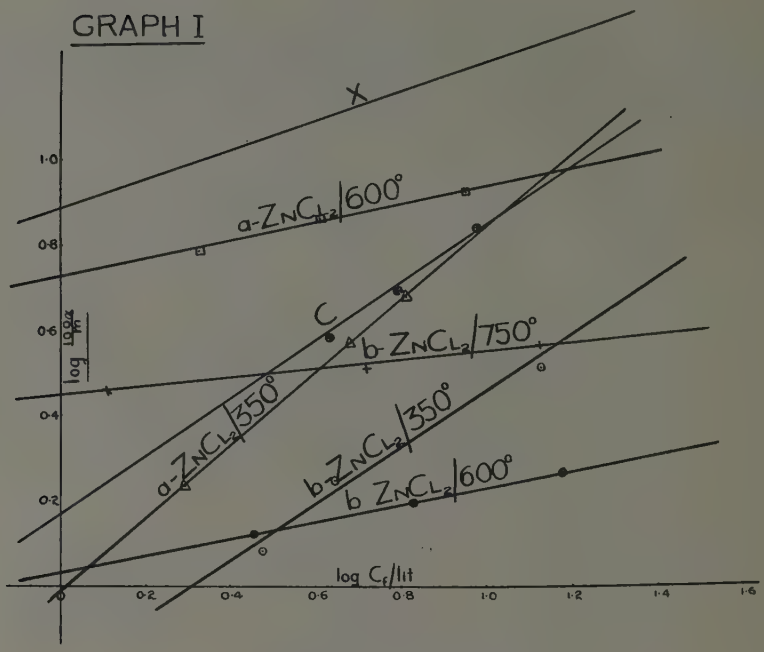
The trend of the figures for the steam-activated charcoals and the abnormality of b-H_3PO_4/950°/30 have already been discussed.

Chaney (J. Ind. Eng. Chem., **15**, 1252, 1923) quotes values from 0·216 to 0·548 for 200–270 mesh fractions of activated charcoals from various sources.

Phenol Isotherms.

1 g. of each charcoal was weighed into small stoppered conical flasks, and distilled water and then phenol (kept as an aqueous solution in a hydrogen atmosphere) added to make a total volume of 20 c.c. After mechanical shaking for 30 minutes each batch of flasks was filtered and the residual phenol in 10 c.c. estimated by titration. The data so obtained were plotted according to the logarithmic form of the adsorption isotherm:

$$\log \frac{100x}{m} = \log k + \frac{1}{n} \log C.$$



Molasses Decolorization.

A filtered solution of molasses was diluted till the colour was brought into a fixed relation with a permanent standard. The specific gravity was 1·01, and the colour fairly dark.

In doing the tests the fresh solution was run into conical flasks containing appropriate weighed amounts of the various carbons. These were kept at 50°–60° in an air oven for 30 minutes with occasional shaking, then filtered and the filtrate poured back once over the paper. The percentage colour remaining was found in a Klett colorimeter, using appropriate sub-standards.

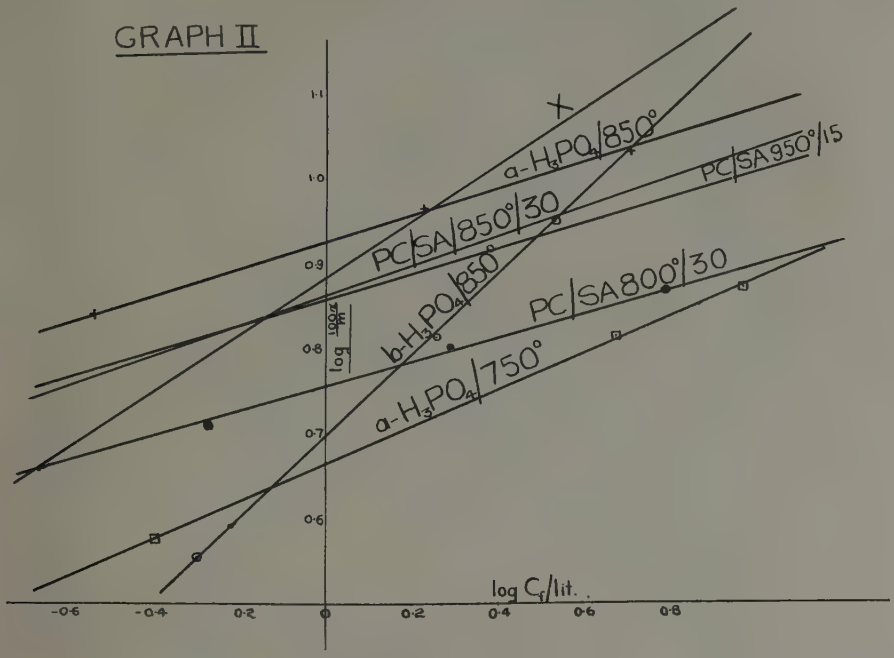
Review of Phenol Isotherms.

The more interesting of these are shown in Graphs I and II. In addition each graph shows the curve for a commercial carbon X, described by its manufacturers as "our quality of highest decolorizing power."

H_2SO_4-activated carbon, C. This was typical of, but slightly better than A and B. Note the steep slope, with the consequent good performance at higher concentrations of phenol.

$ZnCl_2$ charcoals. Note the abnormal behaviour of the 350° charcoals in both groups; the other curves have a much flatter slope and—especially in the

a series—were remarkably similar in properties. Note also the all-round decrease in activity on decreasing the proportion of $ZnCl_2$ used. None of these charcoals is more than fairly good by the commercial standards.



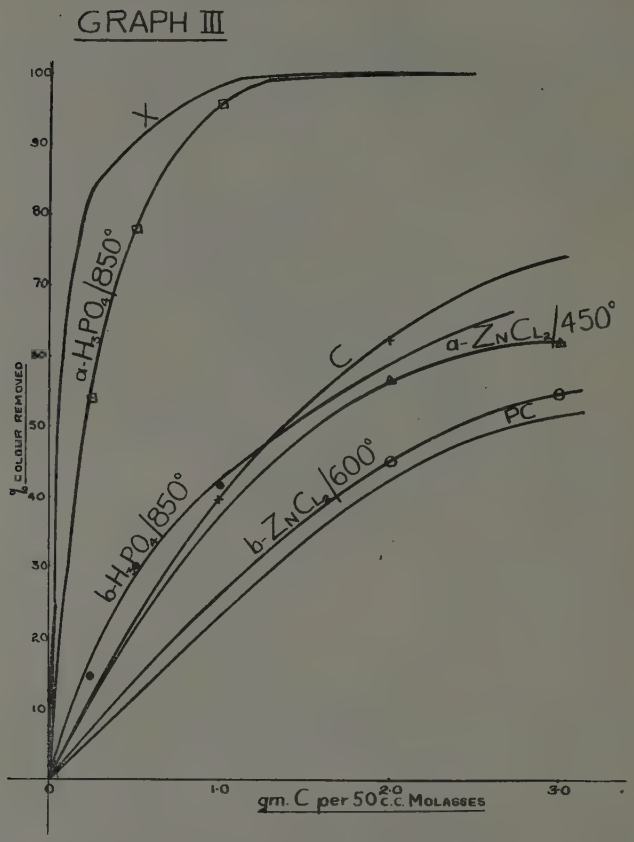
The irregularities in the H_3PO_4-treated carbons make it difficult to draw any general conclusions, except that 750° is obviously too low as a final ignition temperature.

In both the 30-minute and 60-minute steam-activated charcoals the curves for those prepared at 800° showed a much lower adsorptive power than those prepared at higher temperatures. Otherwise there was little difference in behaviour between the other carbons in each group, but the 60-minute charcoals were decidedly inferior to the 30-minute ones. The parallelism between the activities and the bulk densities is noteworthy.

In general, the steam-activated and the H_3PO_4-treated carbons are good by commercial standards, their activity in dilute solutions being remarkably high.

Decolorization of Molasses Solutions.

Here again only a selection of the curves is shown. The other commercial carbon, Y, shown in graph IV is stated by its manufacturers to be "a medium quality decolorizing carbon."



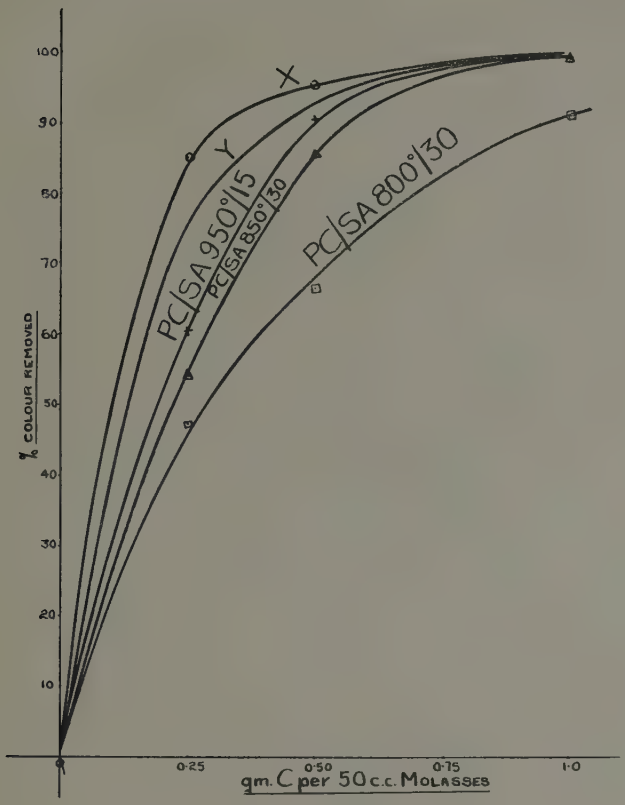
On a basis of equal (90%) decolorization, the primary charcoal, C, and the $ZnCl_2$-treated charcoals are all very disappointing. The H_3PO_4 carbons (except b-H_3PO_4/850°) are reasonably good.

Except in the 800° charcoal, which is again low, the decolorizing powers of the steam-activated charcoals compare well with the commercial standards. Again there is little difference in performance between charcoals prepared at temperatures above 800°.

Summary.

1. Active charcoal has been prepared from peat residue (i.e., peat after removal of the waxy constituents) by a number of methods: activation with warm concentrated sulphuric acid; impregnation with zinc chloride and subsequent carbonization; impregnation with phosphoric acid

GRAPH IV



followed by ignition at high temperatures; and activation with superheated steam.

2. The charcoals prepared, numbering in all about 25, have been examined for the following properties:—percentage yield, appearance and hardness, bulk density, phenol adsorption, and decolorization of molasses solutions.
3. Activation with superheated steam, and, to a lesser extent, by treatment with syrupy phosphoric acid before carbonization, have been found to give charcoals of performance approaching commercial standards.

We wish to thank the staff of the Physics Department, U.C.C., and Mr. J. Mc.Kenna, for assistance on a number of points.

One of us (J. R. O'D.) is further indebted to the Industrial Research Council for a grant enabling this work to be carried out.

No. 38.

THE VITAMIN D REQUIREMENTS OF THE GROWING PIG.

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[Read February 25. Published separately April 10, 1941.]

In a report issued from this Department in 1940 the conclusion was reached that growing pigs require vitamin D even on a high calcium and phosphorus intake with a Ca/P ratio of about 1·4. In recent years workers at some centres have suggested that by keeping the levels and ratios of calcium and phosphorus within certain limits the pig could be made independent of supplies of vitamin D, at least between weaning and bacon weights. In the experiments of last year a single ratio only was chosen, and consequently the conclusions were valid at that ratio only. It was considered desirable, therefore, to carry out further experiments in which other ratios would be adopted. It was decided also to ascertain whether, on the other hand, in the presence of an abundant supply of vitamin D a wide range of ratios of Ca/P was not permissible.

Most workers agree that a level of 0·6% of P in the ration is adequate, provided the calcium content is normal. In fact where abundance of vitamin D is supplied many American investigators have got satisfactory results with P levels not greater than 0·4%. Recommendations vary somewhat regarding the most suitable ratio of Ca to P. Thus Aubel and Hughes (1) found a ratio of 1·5 with a P level of 0·51 better than a ratio of 1·0 with a P level of 0·75. Dunlop (2) found a ratio of 0·78 to be optimal with a P level of 0·59%. Other workers when making up rations seem to favour a ratio of about 1·0. These differences are not serious, and doubtless with adequate vitamin D any of the above ratios would be satisfactory. The object of the present investigation was to find out whether any of them would enable the pig to grow normally to bacon weight in the absence of vitamin D. In the first experiment, therefore, different ratios were chosen which were representative of these recommendations.

Experimental.

Experiment 1 (a).—Effect of absence of direct light with different ratios of Ca to P.

Two Large White sows farrowed on the 22nd December, 1939. During the previous 4 months they had been fed a ration made up of maize meal, bran,

pollard, meat and bone meal, and salt; while the weather permitted they were allowed out on grass each day. The sows reared 16 bonhams in all. Two houses facing north were used, and the doors were kept closed as far as practicable. They were lighted through closed windows in the roof. The sows were out in the open yard each day for several hours except when prevented by severe weather, but the young pigs were confined to the houses at all times. The ration of the sows was the same as during pregnancy. The pigs were weaned on the 16th February at 8 weeks of age. A week later they were divided into three groups, regard being paid to litter, weaning weight, and sex in the usual manner. The weights in lb. were as follows:—37, 38, 33, 28, 23, 32, 30, 28, 36, 29, 41, 39, 40, 27, 27, 29. The average weight was 32 lb. Table 1 shows the basal ration fed. Calcium carbonate in the form of ground limestone was added to the group ration each day in such amounts as adjusted the calcium and phosphorus to the percentages and ratios shown in Table 1.

TABLE 1.—*Basal ration and levels of Ca and P fed in Exp. 1 (a).*

Bran	20 parts		%P	%Ca	Ca/P
Pollard	35 „	Group I ...	0·78	0·59	0·76
Barley meal	30 „	„ II ...	0·78	0·78	1·00
Soya bean meal ...	9 „	„ III ...	0·78	1·19	1·53
Sep. milk powder ...	5 „				
Salt	1 part				

The pigs were fed 3 times daily, the mash being moistened with lime-free water. Ample supplies of vitamin A were given as a concentrate diluted with arachis oil and mixed through their feed. Water was available at all times.

Results.

It may be said at once that rickets developed in all the pigs of all three groups. The first definite symptoms were swelling of the leg joints, and stiffness in gait. Frequent determinations of blood calcium were made, and with the onset of rickets the figure fell from the previous normal level of about 10–11 mg. per 100 ml. of serum to 8 or 7 mg., and occasionally to as low as 6 mg. As soon as the presence of rickets was definitely established the pig was removed from the group, and allowed to get direct light for as long as possible each day. All of them recovered rapidly, and their blood calcium returned to a normal level. The rickety pigs were similar in appearance to those of a previous experiment, photographs of which were published in the earlier communication (3) already referred to.

There was great variation in the times which elapsed between the commencement of experimental feeding and the first symptoms of rickets in the various pigs (Table 2).

TABLE 2.—*No. of days after weaning at which rickets appeared—Exp. 1 (a).*

Group I.	Group II.	Group III.
27	20	23
27	20	23
37	34	25
44	47	30
51	47	30
56	—	—

Of course it was not easy to say at what precise time within a period of 3–4 days the joints first became stiff or swollen. But even allowing for this the variation is very marked. It follows that the figures give no reliable information as to whether there was any difference between the various ratios of Ca to P in their suitability for the needs of the growing pig.

Experiment 1 (b).—Similar to 1 (a).

It was considered desirable to repeat experiment 1 (*a*) under conditions which would be more favourable for the pigs, while maintaining the essential feature of the trial, namely, that they should be dependent chiefly on their mothers' milk for supplies of vitamin D. For this purpose two sows due to farrow in May were selected. One litter was born on the 23rd and the other on the 24th May. The sows had, therefore, the benefit of the long hours of daylight during the latter part of pregnancy and during the 8 weeks of lactation. In addition, during the previous four months their ration included 1% of a good cod liver oil. As before, the sows were allowed out to the yards for several hours each day, but the young pigs were confined to the houses. When weaned at 8 weeks of age there were 9 in each litter. For the purpose of this experiment 4 of the best pigs were selected from each—2 of either sex. The weights of these selected 8 pigs at 9 weeks of age were as follows:—39, 43, 41, 44, 37, 47, 42, 46. They were, therefore, in a thriving condition. They were divided into two groups balanced regarding weight, sex, and litter. The ration was as shown in Table 3. Ground limestone was added to the basal ration in such amounts as adjusted the Ca intake to the figures shown in the table.

TABLE 3.—*Basal ration and levels of Ca and P fed in Exp. 1 (b).*

Bran	20 parts
Pollard	34 „
Maize meal	35 „
Soya bean meal ...	10 „
Salt	1 part

	%P	%Ca	Ca/P
Group I ...	0·64	0·51	0·80
„ II ...	0·64	0·96	1·50

Each group was accommodated in a large house lighted through window glass.

Results.

All 8 pigs developed rickets, and showed the same symptoms as those in experiment 1 (*a*). As soon as they showed stiffness of gait or swollen joints they were removed from the houses, and blood samples taken. In 7 cases the serum calcium was between 6·5 and 8·0 mg. per 100 ml. In the case of the last pig to get rickets it was 8·7 mg. The time taken for development of rickets was very much longer in this experiment, as Table 4 shows.

TABLE 4.—*No. of days after weaning at which rickets appeared—Exp. 1 (b).*

Group I.	Group II.
80	111
84	120
100	127
106	131

It is not possible to say to what factors must be ascribed the freedom from rickets for a much longer period in this experiment as compared with the last. It may be due to the greater potency of the summer sunshine acting on the sows, or even on the young pigs when occasionally they got direct light due to opening of doors, etc. The houses were larger, and as there were only 4 pigs in each group they had more room for exercise. It was noticed that they drank much greater quantities of water right from the beginning of the experiment. Other workers (4) have noticed increased thirst in cases of aphosphorosis, so that possibly blood inorganic P was low also. Since the purpose of the blood analysis in this experiment was merely to confirm the clinical symptoms of rickets, the low values for serum-calcium were taken as providing sufficient evidence. The samples of blood were taken from the ears, and in this case it flowed much more freely even when the pigs had rickets. Possibly this was due to the increased water consumption. It will be observed that Group II on a Ca/P ration of 1·5 were free from rickets for a considerably longer period than Group I on a Ca/P ration of 0·8. The number of pigs in each group, however, was too few to enable a definite conclusion to be drawn. The rate of progress in both groups was very slow even before the onset of rickets. There was no shortage of vitamin A, as all livers contained ample reserves when assayed after death.

It has been suggested (5) that there may be a hereditary factor influencing the quantitative requirements of pigs for vitamin D. The results of these experiments would not conflict with such a theory. It is quite likely, however, that the reserves of the sow herself affect the length of time the offspring will survive in the absence of added vitamin D. An experiment of this type, therefore, in which sows would commence their period of pregnancy with different reserves of vitamin D might throw light on the question as to why

there is such variation between different centres, and even between different pigs in a group, in their powers of resistance to a shortage of vitamin D.

The results of Experiment 1 (*b*) confirm those of 1 (*a*). Their significance is that they show the necessity of supplying vitamin D to the growing pig even though the ration has a P level and a Ca/P ratio which would be described as satisfactory.

Experiment 2.—Effect of different ratios of Ca/P with abundance of vitamin D.

For this trial the progeny of four sows which farrowed between the 22nd and 24th May were utilised. Two of them were those referred to in Experiment 1 (*b*), and the treatment of all four prior to farrowing was similar. There were 10 bonhams available from two of the sows after the 8 had been removed for the purpose of the previous experiment, and the other two sows reared 16. At 8 weeks of age they were finally weaned, and the 26 young pigs divided over 4 groups in the usual way. The basal ration used and the Ca and P levels, adjusted as before by the addition of ground limestone, are shown in Table 5.

TABLE 5.—*Basal ration and levels of Ca and P fed in Exp. 2.*

Bran	10 parts		%P	%Ca	Ca/P
Pollard	29 „	Group I ...	0·55	0·28	0·5
Maize meal	50 „	„ II ...	0·55	0·55	1·0
Soya bean meal ...	10 „	„ III ...	0·55	0·83	1·5
Salt	1 part	„ IV ...	0·55	1·10	2·0

Cod liver oil was added to the ration at the rate of 1 pint per cwt. The pigs had access each day to open yards adjacent to their houses. They had, therefore, abundance of vitamins A and D. Unfortunately, in the third week of the experiment, an outbreak of swine influenza occurred among the pigs. At the first signs of illness the affected pigs were removed from the groups for treatment. Of 8 pigs so removed 2 died, and the others made very poor progress. It is worth recording that of the 8 cases of severe influenza 7 occurred amongst the progeny of the 2 sows whose litters were reared in the absence of direct light. While the design of this experiment would not justify a general statement as a result of this observation, the distribution is certainly suggestive.

Results.

There was no sign of rickets in any group. At no time did the animals show stiffness of gait or swollen joints. Neither did post-mortem examination of the joints show any abnormalities. The level of calcium in the blood was determined monthly in the case of Groups I and IV and at the conclusion of

the experiment on all pigs. The figures were normal in all cases. Table 6 gives the result of the blood analysis at the end of the experiment.

TABLE 6.—*Serum calcium at 33 weeks of age* (mg./100 ml.).

Group I.—Ca/P = 0·5.	Group III.—Ca/P = 1·5.
10·1	10·3
9·8	9·5
9·9	11·1
10·2	10·2
9·9	10·8
10·0	9·4
	10·9
Group II.—Ca/P = 1·0.	**Group IV.—Ca/P = 2·0.**
10·2	10·4
11·0	11·6
9·8	10·9
10·3	12·7
10·5	10·7
10·9	

Rickets was not to be expected in Groups II or III, as ratios of Ca to P of 1·0 and 1·5 with a P level of 0·55% would be generally considered satisfactory. The ratio of 0·5 in Group I gave a Ca level of only 0·28%, which must be close to the minimum, even in the presence of abundant vitamin D. Also, in Group IV it would not have been surprising had a ratio of 2·0 with a P level as low as 0·55% brought about disorders in the metabolism of these minerals. The figures give no indication, however, of hypercalcaemia.

These results demonstrate the great potency of vitamin D in compensating a disequilibrium in the calcium and phosphorus content of a ration.

It does not follow that, from the view point of live-weight increase and economy of gain, all these ratios would be equally good. In designing the experiment it was hoped that the weight record of the pigs would indicate whether some ratios were slightly better than others. The outbreak of influenza, however, prevented this. If the records of those pigs which suffered a severe attack are neglected there are too few animals left in some of the groups to justify the use of a figure for an average live-weight increase. Also, it is probable that other pigs besides those showing very obvious symptoms suffered a set-back in their progress. While, therefore, this experiment may not indicate an optimum ratio, it does prove, as already stated, that with adequate vitamin D the Ca/P ratio may vary within the rather wide limits chosen, without any pathological condition developing.

SUMMARY AND CONCLUSION.

Pigs were reared from birth in the absence of direct light. In the first experiment with 3 groups (16 pigs in all), the P content of the ration was 0·78% and the Ca/P ratios were 0·76, 1·00, and 1·53. In the second experiment of 2 groups (8 pigs in all), the P level was 0·64% and the Ca/P ratios 0·80 and 1·50. In all cases rickets developed at ages varying from 4–6 months.

In another experiment 4 groups were reared on rations containing 0·55% P with Ca/P ratios of 0·5, 1·0, 1·5, and 2·0. Sunlight and cod liver oil supplied vitamin D. In no case did rickets develop.

No adjustment of the calcium or phosphorus content of a ration will render the pig independent of supplies of vitamin D. Conversely, with adequate amounts of vitamin D, the calcium to phosphorus ratio may vary within wide limits without causing a pathological condition to develop.

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1.—Dissemination of Potato Viruses X and F by Leaf Contact. By J. B. LOUGHNANE and PAUL A. MURPHY, Albert Agricultural College, Glasnevin, Dublin. 1s. 6d. (May, 1938.)

2.—A Study of the Infiltration of Viruses into Seed Potato Stocks in the Field. By PHYLLIS CLINCH, J. B. LOUGHNANE, and PAUL A. MURPHY. 1s. 6d. (June, 1938.)

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